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## OZONE CONTROL AND VOC REACTIVITY

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Tropospheric ozone is not emitted, but is formed in the atmosphere through a complex, nonlinear process involving volatile organic compounds (VOCs), oxides of nitrogen (NO and NO<sub>2</sub>, with the sum denoted as NO<sub>x</sub>), and sunlight. Anthropogenic emissions have led to urban ozone levels far exceeding those believed to be safe for human health and the environment. Although great efforts have been made to reduce urban ozone levels, concentrations remain high. However, a promising new technique for use in the development of ozone control strategies is emerging. This technique is based on accounting for the ozone-forming potential, termed *reactivity*, of individual VOCs. This technique helps to identify the most reactive emission sources and aids in targeting specific VOCs for reduction. Reactivity-based emissions reduction is most effective in highly polluted, NO<sub>x</sub>-rich urban areas and should often be applied in conjunction with reduction of NO<sub>x</sub> emissions. NO<sub>x</sub> emissions reduction is the optimum ozone control strategy for areas where ozone formation is limited by the availability of NO<sub>x</sub>.

The following sections present this control strategy technique by first discussing the background of tropospheric ozone, including ozone and its effects, and the history of ozone trends and regulation in the United States. Next, the chemistry of ozone formation is presented, followed by discussions of the scientific basis and policy implications in VOC reactivity quantification, of uncertainties in VOC reactivity quantification and

issues in regulatory application, and, finally, of ozone reduction through VOC reactivity-based control strategies.

## OZONE AND ITS EFFECTS

Ozone ( $O_3$ ) is a highly reactive trimeric state of oxygen that occurs naturally in the earth's atmosphere. Ozone is not directly emitted, but is formed through reactions of VOCs and  $NO_x$  in the presence of sunlight. In the stratosphere, ozone serves the important function of blocking the earth from harmful UV radiation. In the troposphere, it behaves as a highly reactive oxidant. Ozone concentrations between 10 and 40 parts per billion (ppb) occur naturally in a clean troposphere through both stratospheric injection and chemical reactions of  $NO_x$  with biogenic organic compounds. (Parts per billion (or parts per million) often represents concentration defined as a mixing ratio (ie, ppb or ppm by volume)). However, in polluted urban areas, ozone concentrations often reach between 100 and 300 ppb (1), with some severely affected areas experiencing even higher levels. Ozone and its precursors can be transported over large regions. Elevated ozone concentrations are believed to be responsible for a wide range of adverse environmental and health impacts.

Determination of the impacts of exacerbated ozone levels is complicated by variability in exposure and by interactions between ozone and other air pollutants such as sulfur dioxide ( $SO_2$ ) and particulate matter (PM). However, a large body of research results gives the strong indication that ozone is responsible for damage to human health, crops, and natural vegetation. In addition, tropospheric ozone is a greenhouse gas, which contributes to global climate change (2,3).

Ozone is believed to be responsible for acute and chronic impacts on human health, especially on lung functions, asthma exacerbations, and clinic visits and hospital admissions for respiratory diseases. Human health impacts are the primary consideration in air quality standards, which are based on effects on sensitive populations. The most sensitive populations to ozone are children and people with a preexisting respiratory disease such as asthma (4). People who exercise or work outdoors are also considered to be at special risk because of the combined effect of outdoor exposure and physical exertion, which increases the amount of ozone inhaled and the depth of its penetration into the lungs, and thereby susceptibility to ozone (2,5). However, much evidence indicates that ozone can adversely affect the respiratory systems of any individual depending on the conditions of exposure (6). Major acute (short-term) effects of ozone are decreased lung function and increased susceptibility to respiratory problems such as asthma attacks and pulmonary infection. Short-term exposure can also cause eye irritation, coughing, and breathing discomfort (5-7). Evidence of acute effects of ozone is believed to be clear and compelling (8).

Chronic (long-term) health effects may present a potentially far more serious problem; however, definitive evidence is difficult to obtain because of uncertainties associated in examining human populations (because of variables in exposure and behaviors), as well as uncertainties in the extrapolation of animal toxicology experiments to humans. Recent controlled-exposure human studies demonstrate that ambient levels of ozone induce inflammation in human lungs, which is generally accepted as a precursor to irreversible lung damage (6). Also, chronic animal exposure studies at concentrations

within current ambient peak levels indicate progressive and persistent lung function and structural abnormalities (5,8).

Crop damage caused by air pollution has also received much attention. It is estimated that 10-35% of the world's grain production occurs in regions where ozone pollution likely reduces crop yields (9). Air pollution accounts for an estimated several billion dollar crop loss every year in the United States alone, and research and analysis suggests that about 90% of this crop loss can be directly or indirectly attributed to ozone (10). Evidence also indicates that ozone may cause short- and long-term damage to the growth of forest trees (11), as well as altering the biogenic hydrocarbon emissions of vegetation (12). Preliminary research is also addressing ozone effects on sensitive wildlife populations, such as amphibians; however, there are no conclusions to date.

Permissible levels of ozone in the United States are specified in a National Ambient Air Quality Standard (NAAQS). The primary standard is based on human health effects, and is currently a 1-hour average concentration of 120 ppb, not to be exceeded more than once per year. From 1991-1993, an estimated 60 million individuals in the United States (24% of the U.S. population) resided in areas that violated this NAAQS (4). Although this represents an improvement over the estimated 112 million individuals exposed in 1986-1988 (7), ozone remains a serious health risk. Many urban areas outside of the United States also often experience ozone levels far exceeding the current U.S. NAAQS. Additionally, many scientists strongly believe the current U.S. NAAQS does not contain a sufficient margin of safety to protect human health (5,7,13). The U.S. Environmental Protection Agency (EPA) has proposed a revised ozone NAAQS (U.S. EPA, Ozone A-95-58) based on a maximum 80 ppb average concentration over an 8-hour period. As proposed, the three-year average of the annual third highest daily maximum concentration must not exceed the 80-ppb limit. Final action on this proposed NAAQS revision is expected during July 1997.

No matter what level of ozone is eventually deemed acceptable, the emissions reductions required will be difficult to identify and costly to implement. Great efforts have been made in the United States during the past 40 years to reduce urban ozone, but these efforts have been less than fully successful. Any control strategy that can focus emissions reduction efforts will help in meeting the air quality goals, and quantification of VOC reactivity is proving to be a very promising technique for refining urban ozone control strategies.

## HISTORY OF OZONE REGULATION IN THE UNITED STATES

The history of ozone regulation in the United States is highlighted by year and event in Table 1. In 1963, the Clean Air Act (CAA) became the first modern environmental law to be enacted by the US Congress. Major amendments were made to the 1963 original legislation in 1970, 1977, and 1990. The CAA establishes the federal/state relationship that requires the EPA to develop uniform national ambient air quality standards (NAAQS) and empowers the states to implement and enforce regulations to attain them.

In the CAA amendments of 1970, Congress set a deadline of 1975 for meeting the NAAQS for ozone. However, in 1977, two years after the deadline, many areas throughout the country were still not in attainment of the ozone standard. The 1977

Table 1. History of Ozone Regulation in the United States<sup>a</sup>

Year	Event
1943	The first recognized episode of smog occurs in Los Angeles on Sept. 8. People report smarting eyes, respiratory discomfort, nausea, and vomiting.
1945	World War II ends. Urban sprawl begins to take root in much of the United States.
1950	More than 100 electric transit systems are replaced with buses in 45 US cities, including Los Angeles.
1952	Dr. A. Hagen-Smit discovers the nature and causes of photochemical smog.
1955	The Air Pollution Control Act is passed.
1960	The Motor Vehicle Act is enacted. It requires research to address pollution from motor vehicles.
1963	The first Clean Air Act is passed. The Act empowers the Secretary of Health, Education, and Welfare to define air quality criteria based on scientific studies and provides grants to state and local air pollution control agencies. Major automobile manufacturers install the first crankcase control devices on 1963 model year cars.
1964	Chrysler receives approval for an exhaust control system.
1965	The CAA is amended by the Motor Vehicle Air Pollution Control Act. It provides for direct regulation of air pollution.
1967	The Air Quality Act is enacted. It establishes framework for defining air quality control regions based on meteorological and topographical factors.
1970	The U.S. EPA is created. The CAA Amendments are enacted and serve as the principal source of statutory authority for controlling air pollution.
1971	U.S. EPA establishes NAAQS.
1975	First two-way catalytic converters come into use.
1976	Volvo introduces the first three-way catalytic converter to control hydrocarbons, NO <sub>x</sub> , and carbon monoxide emissions from 1977 model year cars.
1977	The Clean Air Act Amendments are enacted and require review of all NAAQS by 1980.
1990	More CAA Amendments are enacted. New programs are established to control urban ozone, rural acid rain, stratospheric ozone depletion, toxic air pollutants, and vehicle emissions.
1995	Reformulated gasoline comes to market.
1996	The big seven auto makers commit to manufacture and sell zero-emission vehicles.

<sup>a</sup> Adapted from Ref. 15.

amendments to the CAA delayed compliance until 1982, and areas that demonstrated that they could not meet the 1982 deadline received extensions until 1987. In 1990, three years after the final deadline, more than 133 million Americans were living in 96 areas that had not met the NAAQS during the previous year (14). In Los Angeles, for example, peak ozone levels were 175% above the NAAQS.

The latest amendments to the CAA, adopted in 1990, classify nonattainment areas according to the degree of non-compliance with the NAAQS. The regions are classified as extreme, severe, moderate, or marginal, depending on the area's ozone design value. Ozone design values are ozone concentrations that are statistically determined from air quality measurements for each area. If monitoring for an area is complete, the design value is the fourth highest monitor reading taken during the past three years. Only one area is

classified as extreme, the South Coast Air Basin (Los Angeles and surrounding communities), and it has 20 years from 1990 to attain the NAAQS. The severe areas are in four major areas of the nation: the Northeast Corridor (which extends from Washington, DC, to Maine); the Chicago area, including downwind areas in Wisconsin and Michigan; the greater Houston area; and San Diego. These areas have 17 years to reach attainment of the ozone standard.

The State Implementation Plan (SIP) is the technical and regulatory process for demonstrating attainment and maintenance of the requirements of the NAAQS. SIPs must be adopted by local and state governments and then approved by EPA. Once approved by EPA, the plan is legally enforceable under state and federal law, which makes the SIP a powerful tool for achieving the NAAQS.

VOCs and NO<sub>x</sub> emitted from motor vehicles, local industries, and additional sources are the primary cause of excessive levels of ozone. Except in California, most SIPs have relied entirely on VOC control to attain the NAAQS, allowing NO<sub>x</sub> emissions to remain the same or to increase with population and industrial growth. Despite considerable resource investment by industry since the promulgation of the NAAQS, most large cities do not meet the ozone standard. Various new directions are being explored to find more effective control strategies. One path, controlling NO<sub>x</sub> emissions instead of VOC emissions, appears to be most effective for regional transport problems, in rural areas, and in urban areas with high VOC to NO<sub>x</sub> ratios (eg, regions with large emissions of biogenic VOC). However, in the largest urban areas with the worst ozone problems, reductions of VOC are effective. In recognition of California's success in reducing ozone levels through a policy of reducing both VOC and NO<sub>x</sub> emissions, the 1990 amendments to the CAA allow states (with EPA guidance and approval) to supplement or replace VOC controls with NO<sub>x</sub> controls if a benefit can be demonstrated. Estimates of control costs needed to attain the ozone NAAQS are on the order of billions of dollars per year. In the most severely affected regions of the United States (Los Angeles, for example), the necessary control technologies have not been identified completely (16).

Past VOC regulations implicitly assumed that all tons of emissions produce equivalent amounts of ozone in the urban atmosphere. However, ozone-forming potentials of VOCs can vary significantly. Among almost 300 organic species identified in the urban atmosphere, some species, such as alkenes, most aromatic VOCs, and aldehydes, can lead to an order of magnitude greater ozone formation than equivalent amounts of other VOCs, such as alkanes, benzene, alcohols, and ethers. Such disparities in emissions impacts have tremendous implications as NAAQS nonattainment areas consider strategies to tighten VOC controls. Such strategies include reformulation of surface coatings and transportation fuels, regulation of consumer products, and development of VOC emissions trading programs. To aid in understanding some of the difficulties in identifying effective emissions reductions for ozone control, the following section discusses the process of ozone formation, and the tools used to predict how changes in emissions affect ozone.

## PROCESS AND PREDICTION OF OZONE FORMATION

### Chemistry of Ozone Formation

Ozone formation in the troposphere results from complex interactions among NO<sub>x</sub> and VOCs (1,2). Apart from remote regions,

where the in situ tropospheric chemical generation of ozone is driven essentially by methane (17), a relatively large number of VOCs participate in ozone generation. Measurements of nonmethane organic compounds in the South Coast Air Basin of California during the 1987 Southern California Air Quality Study, for example, revealed more than 280 hydrocarbon and oxygenated organic species, many of which contribute to some degree to ozone generation (18).

Although VOCs impact the formation of ozone, they do not directly create it. As explained in more detail subsequently, ozone is produced and destroyed in a reaction cycle with  $\text{NO}_x$  that is driven by sunlight, and VOCs can interfere with the ozone destruction reactions in this cycle. VOCs react in a number of different ways; however, the dominant tropospheric reactions for VOCs are with the hydroxyl (OH) radical. These VOC-OH reactions often lead to the conversion of NO to  $\text{NO}_2$  without the use of an ozone molecule. Additionally, individual VOCs follow different reaction pathways, and therefore vary widely in their ozone-forming capability. As discussed later, smog chamber experiments carried out with a series of single hydrocarbons irradiated in the presence of  $\text{NO}_x$  clearly indicate differences in ozone formation from individual hydrocarbons. Hydrocarbons do not occur singly in the atmosphere, however, and the ozone-forming potential of an individual VOC will depend on the characteristics of the complex mixture of which it is a part, including the  $\text{NO}_x$  level and the other VOCs that are present. For example, Table 2 shows the percentage of ozone production attributable to a number of VOCs under various VOC-to- $\text{NO}_x$  ratios, representing different urban atmospheric conditions, as calculated using a single-cell air quality model (19). As seen in this table, not only do the VOCs have varying ozone forming potentials, but this potential varies with background VOC-to- $\text{NO}_x$  ratios.

The only significant process forming  $\text{O}_3$  in the lower atmosphere is the photolysis of  $\text{NO}_2$  (reaction with sunlight), followed by the rapid reaction of the oxygen atoms formed with  $\text{O}_2$ .



This is reversed by the rapid reaction of  $\text{O}_3$  with NO:



This cycle results in  $\text{O}_3$  being in a photostationary state (in which concentrations depend on the amount of sunlight available) dictated by the  $\text{NO}_2$  photolysis rate ( $k_1$ ) and the  $[\text{NO}_2]/[\text{NO}]$  ratio.

$$[\text{O}_3]_{\text{steady-state}} = \frac{k_1[\text{NO}_2]}{k_2[\text{NO}]} \quad (3)$$

Because of this  $\text{NO}_x$ -dependent photostationary state, ozone levels generally rise and fall with the sun, behavior that is referred to as *diurnal*.

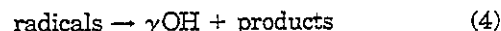
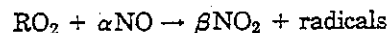
If the above  $\text{NO}_x$  cycle were the only chemical process at work, the steady-state concentrations of ozone would be relatively low. However, when VOCs are present, they react to form radicals that either consume NO or convert NO to  $\text{NO}_2$ , which, because of the photostationary state relationship described by equations 1 and 2, causes  $\text{O}_3$  concentrations to increase. VOCs are emitted by both biogenic and anthropogenic sources. Al-

Table 2. Percentage of Ozone Production Attributable to each Organic<sup>a</sup>

Organic	VOC/ $\text{NO}_x$ , ppb C/ppb			VOC in Emissions, %
	4	8.2	20	
Carbon monoxide	4.7	5.9	5	34.9
Methane	0.5	0.8	0.8	39.5
<i>Aldehydes and Ketones</i>				
Formaldehyde	1.8	1.2	1.3	0.2
Acetaldehyde	1.3	1	0.9	0.1
Propionaldehyde and lumped higher aldehydes	0.4	0.3	0.3	0.04
Methylethyl ketone and lumped higher ketones	0.6	0.6	0.5	0.4
<i>Alkanes</i>				
Lower lumped alkanes	11.1	16.7	16.7	8.2
Higher lumped alkanes	12.6	16.3	17.2	5.5
<i>Aromatics</i>				
Lower lumped aromatics	5.6	5.5	5.3	3.4
Higher lumped aromatics	17.7	12.8	12.9	2.5
<i>Alkenes</i>				
Ethene	10.8	12.3	11.8	1.7
Lumped higher alkenes 1	13	11.5	11.9	1.4
Lumped higher alkenes 2	6.8	5.4	5.3	0.7
Lumped higher alkenes 3	12.8	9.6	10.2	1.5
Total peak ozone (ppb)	58	378	303	NA

<sup>a</sup> Ref. 19.

though many types of reactions are involved (1,2,20,21), for most VOCs the major processes can be summarized as follows:



Destruction of NO and production of  $\text{NO}_2$  and OH radicals ( $\alpha$ ,  $\beta$ , and  $\gamma$ , respectively), and hence the rate of ozone increase caused by these processes, are dependent on the rate constant of the VOC initial reaction, on the amounts of VOCs present, the level of OH radicals and other species with which the VOCs might react, and ambient conditions. Ozone production continues as long as sufficient  $\text{NO}_x$  is present so that reactions of peroxy radicals ( $\text{RO}_2$ ) with NO compete effectively with their reactions with other peroxy radicals.

Note that the OH radical levels are particularly important in affecting the  $\text{O}_3$  formation rate in the presence of  $\text{NO}_x$  because reaction with OH is a major (and in many cases the only) process that causes most VOCs to react. Thus, if a VOC reacts in such a way that it initiates radical levels (or forms a product that does), it would enhance the rate of ozone formation from all VOCs present. This would result in a larger effect on  $\text{O}_3$  than other VOCs that react at the same rate. If the

VOC reactions in the presence of  $\text{NO}_x$  have a radical termination process, it will cause all other VOCs to react more slowly and form less  $\text{O}_3$ . In some cases, this reduced  $\text{O}_3$  formation from other VOCs may be more than enough to counter the ozone formation from the VOC direct reactions. In such cases the VOC would have a negative effect on the formation of  $\text{O}_3$  in the presence of  $\text{NO}_x$  (22,23).

Although an OH reaction is the major atmospheric loss process for most VOCs, some VOCs are also consumed to a nonnegligible extent by reaction with  $\text{O}_3$  or  $\text{NO}_3$  or by direct photolysis. In most cases, these processes will also form  $\text{RO}_2$  radicals, which convert NO to  $\text{NO}_2$ . In addition, and perhaps more significantly, many of these processes initiate the formation of new radicals, which ultimately cause higher OH radical levels and thus higher rates of reactions of the other VOCs present. This is particularly significant in the case of compounds that can photolyze, because photolysis reactions are the main sources of radicals in photochemical smog. For example, it is because of photolysis that formaldehyde has a much larger effect on ozone than one would estimate based on its OH rate constant alone.

Ozone formation stops once  $\text{NO}_x$  is consumed to sufficiently low levels. Because the  $\text{NO}_x + \text{OH}$  rate constant exceeds that of most hydrocarbon + OH rate constants, and because the  $\text{NO}_x$  removal processes generally involve a single step (such as the reaction of OH with  $\text{NO}_2$ ), whereas most VOC reactions form products which are also reactive VOCs,  $\text{NO}_x$  is removed from the atmosphere more rapidly than VOCs. Therefore,  $\text{NO}_x$  availability ultimately limits  $\text{O}_3$  formation. If the  $\text{NO}_x$  levels are high enough that it is not consumed before the end of the day, then it is mainly the rate of the VOC reactions, and their effects on OH radicals, which affect ozone levels. Indeed, high levels of  $\text{NO}_x$  inhibit  $\text{O}_3$  because reaction of OH with  $\text{NO}_2$  reduces OH levels. If, however,  $\text{NO}_x$  is consumed before the end of the day,  $\text{O}_3$  is  $\text{NO}_x$ -limited, and increasing  $\text{NO}_x$  would cause increased  $\text{O}_3$  formation. Under such conditions, if VOC reactions caused  $\text{NO}_x$  to be removed more rapidly than if the VOC were absent (eg, by forming nitrogen-containing products such as PAN from aldehydes and nitrophenols from aromatics), this would have a negative effect on  $\text{O}_3$  yields, and tend to reduce the amount of  $\text{O}_3$  formation caused by the VOCs reactions. Under highly  $\text{NO}_x$ -limited scenarios, this becomes sufficiently important to cause VOCs with significant  $\text{NO}_x$  sinks in their mechanisms to have negative effects on final  $\text{O}_3$  yields, even for those that may have highly positive effects on  $\text{O}_3$  under conditions where  $\text{NO}_x$  is plentiful.

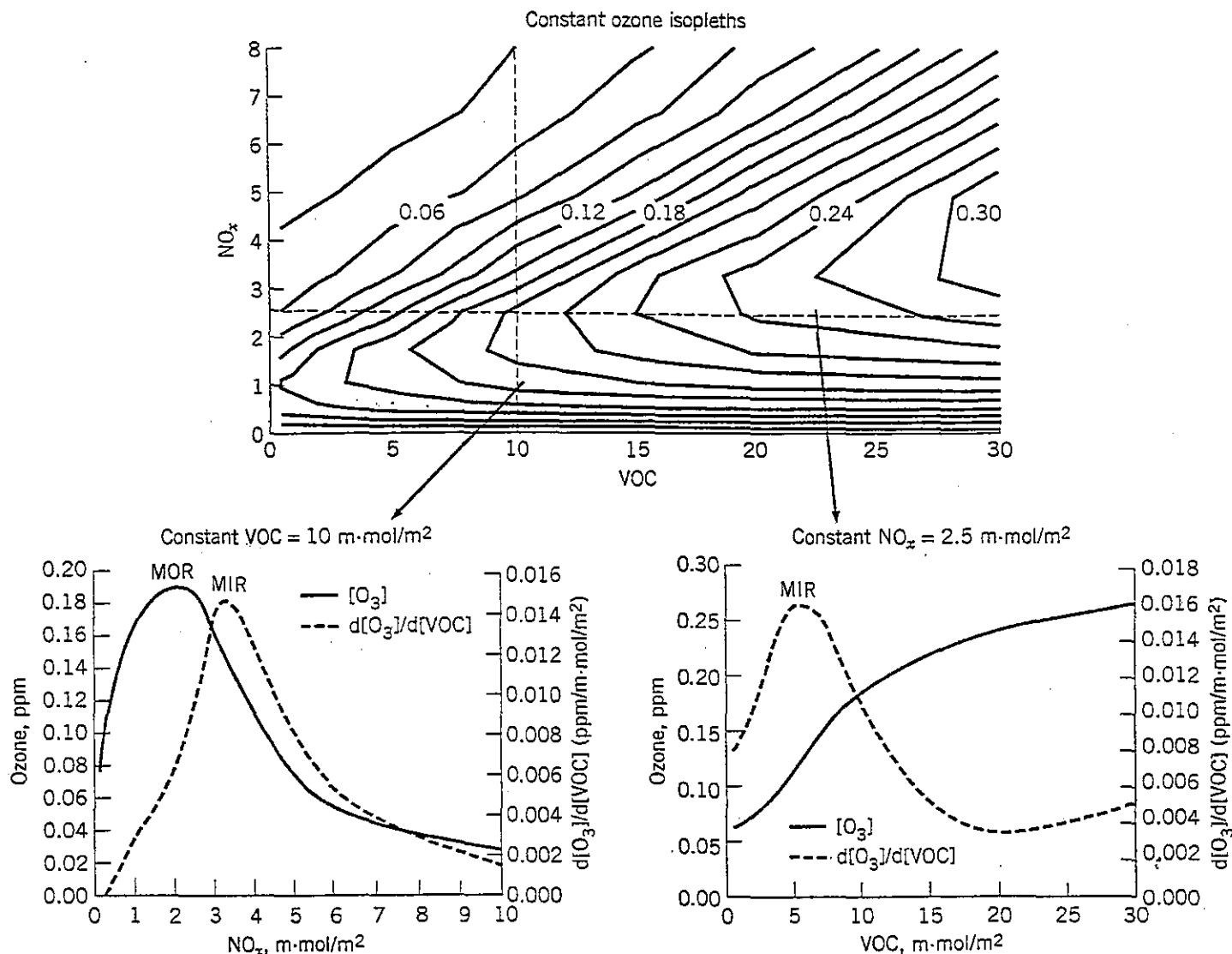
Another factor affecting the behavior of VOCs and  $\text{NO}_x$  in ozone formation is competition for the hydroxyl radical. When the instantaneous VOC-to- $\text{NO}_2$  ratio is sufficiently low, OH reacts predominantly with  $\text{NO}_2$ , removing radicals and retarding ozone formation. Under these conditions, a decrease in  $\text{NO}_x$  concentration favors ozone formation. At a sufficiently low concentration of  $\text{NO}_x$ , or a sufficiently high VOC-to- $\text{NO}_2$  ratio, a further decrease in  $\text{NO}_x$  favors peroxy-peroxy reactions, which retard ozone formation by removing free radicals from the system. Although, in general, higher VOC concentrations mean more ozone, increasing  $\text{NO}_x$  may lead to either more or less ozone depending on the prevailing VOC-to- $\text{NO}_x$  ratio. As a result, the rate of ozone production is not simply proportional to the amount of  $\text{NO}_x$  present; at a given level of VOC, there exist an  $\text{NO}_x$  concentration at which a maximum amount of ozone is produced, or an optimum VOC-to- $\text{NO}_x$  ratio. By using an av-

erage VOC-OH reaction rate constant, representing reactions occurring in an average urban mix of VOCs, the ratio of the OH- $\text{NO}_x$  to OH-VOC rate constants is about 5.5. Thus, this optimum VOC-to- $\text{NO}_x$  ratio is approximately 5.5:1 for an average urban area, with the VOC concentration expressed on a carbon atom basis. For ratios less than this optimum ratio,  $\text{NO}_x$  increases lead to ozone decreases, whereas at ratios higher than this optimum ratio,  $\text{NO}_x$  increases lead to ozone increases.

VOC-to- $\text{NO}_x$  ratios sufficiently low to retard ozone formation from that at the optimum ratio can occur in central cities with  $\text{NO}_x$  sources and in plumes immediately downwind of  $\text{NO}_x$  sources. Rural environments tend to be characterized by fairly high VOC-to- $\text{NO}_x$  ratios because of the relatively rapid removal of  $\text{NO}_x$  from non-local sources as compared to that of VOCs (coupled with the usual absence of strong local  $\text{NO}_x$  sources). Indeed, in most of the troposphere, except in areas of strong sources of  $\text{NO}_x$ , the availability of  $\text{NO}_x$  governs ozone production.

The previously described dependence of  $\text{O}_3$  production on the initial amounts of VOC and  $\text{NO}_x$  is frequently represented by means of an ozone isopleth diagram. An example of such a diagram is shown on the top portion of Figure 1. The diagram is a contour plot of maximum ozone concentrations achieved over a fixed time of irradiation as a function of initial VOC and  $\text{NO}_x$  concentrations. The diagram is generated by contour plotting the predicted ozone maxima obtained from a large number of air quality model simulations with an atmospheric VOC- $\text{NO}_x$  chemical mechanism. Initial concentrations of VOC and  $\text{NO}_x$  are varied; all other variables are held constant. (Air quality models and chemical mechanisms are both discussed in more detail in the following sections.) Notice that there is a ridge along a certain VOC-to- $\text{NO}_x$  ratio where the highest ozone concentrations occur at given VOC levels. This is the optimum VOC-to- $\text{NO}_x$  ratio mentioned previously.

Cross sections of the isopleth plots are shown on the bottom plots on Figure 1. These plots also show the derivatives of ozone formation with respect to initial VOC levels (that is, how much the ozone changes when the initial VOC levels are increased by a given amount). This provides a measure of the sensitivity of ozone formation to changes in VOC emissions, and a measure of VOC reactivity, as discussed in more detail subsequently. Notice that ozone levels monotonically increase as VOC increases (bottom-right plot), but as discussed, there is an optimum  $\text{NO}_x$  level for ozone formation in the presence of a given amount of VOC (bottom-left plot). Lower  $\text{O}_3$  is formed at high  $\text{NO}_x$  because of the competition for OH radicals, and lower  $\text{O}_3$  is also formed at low  $\text{NO}_x$  because  $\text{O}_3$  becomes  $\text{NO}_x$ -limited. The sensitivity of ozone to VOCs has a peak value at a given VOC-to- $\text{NO}_x$  ratio regardless of whether VOC or  $\text{NO}_x$  are varied, indicating that there is a certain ratio where ozone is most sensitive to changes in VOC emissions. Note that the VOC-to- $\text{NO}_x$  ratio where ozone is most sensitive to VOC emissions is lower than the ratio that is optimum for ozone formation. This is shown most clearly on the bottom-left plot on Figure 1, where the peak for the plot of the change in ozone with a change in VOC ( $d[\text{O}_3]/d[\text{VOC}]$ ) occurs at a higher  $\text{NO}_x$  level (lower VOC-to- $\text{NO}_x$  ratio) than the plot of the amount of ozone formed ( $[\text{O}_3]$ ). The VOC and  $\text{NO}_x$  conditions that are most favorable for peak ozone formation (the maximum  $[\text{O}_3]$ ), and those that are most sensitive to changes in VOC emissions (the maximum  $d[\text{O}_3]/d[\text{VOC}]$ ), are referred to as maximum ozone reactivity (MOR), and as maximum incremental



**Figure 1.** Dependences of peak ozone and  $d[\text{O}_3]/d[\text{VOC}]$  on VOC and  $\text{NO}_x$ ; MOR, maximum ozone reactivity, also referred to as maximum ozone incremental reactivity (MOIR); MIR, maximum incremental reactivity. One day maximum ozone concentrations calculated in a one-day box model simulation using the "averaged conditions" scenario of (23) and the SAPRC-93 chemical mechanism.

reactivity (MIR) conditions, respectively. Discussed subsequently, this concept is useful for developing VOC reactivity scales.

From this analysis we see that  $\text{NO}_x$  conditions are a major factor determining the impact of VOC emissions on ozone. However, other conditions will also affect VOC reactivity, by affecting how rapidly  $\text{NO}_x$  is removed, by affecting overall radical levels (and thus how rapidly  $\text{NO}_x$  and VOCs react), and by affecting other factors determining the efficiency of ozone formation. This results in variations of VOC reactivities among different airshed conditions, even those with similar  $\text{NO}_x$  levels. These issues are discussed in more detail in a later section.

#### Air Quality Models

Air quality models, also called airshed models, are computerized representations of the atmospheric processes responsible for air pollution, which includes ozone formation. These models are essential to evaluating control strategies aimed at reducing pollution to meet air quality goals. Figure 2 is a schematic showing how air quality modeling is used for evaluation of control strategies. For pollutants that are emitted directly, such as carbon monoxide, the models are primarily useful for predicting how the pollutants are distributed once they are emitted, and how rapidly they disperse. If the pollutant is formed in the atmosphere rather than being emitted directly, as is the

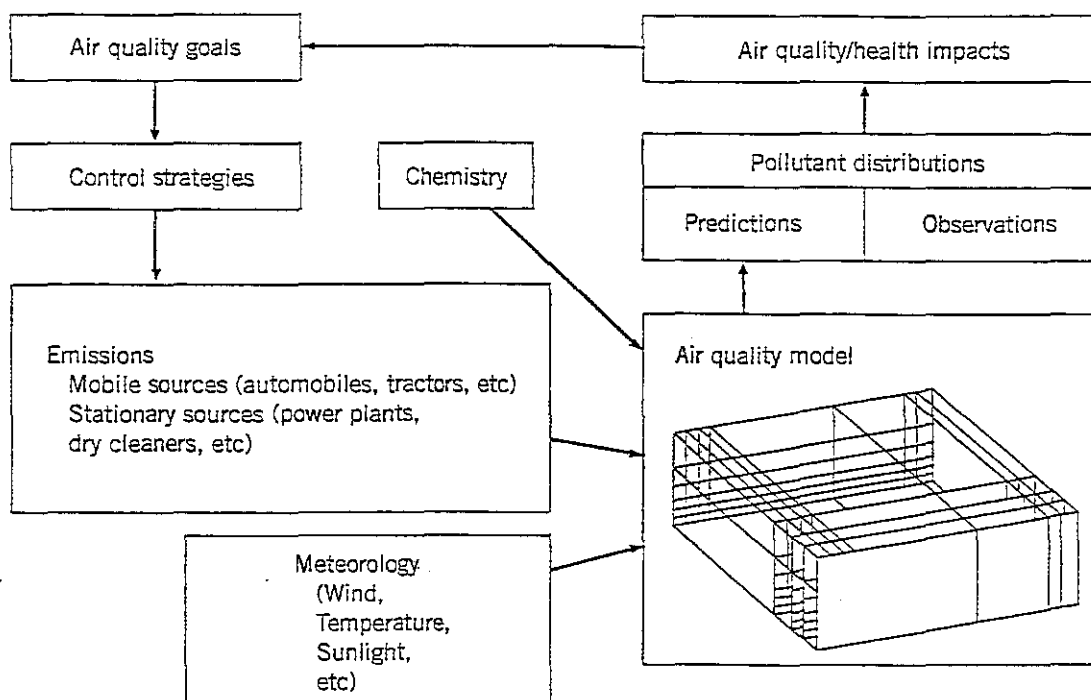


Figure 2. Air quality modeling for atmospheric impact analysis.

case for ozone, the model must predict the distribution and transport of the precursors, the speed with which the pollutant is formed from its precursors, its resulting distribution and transport once formed, and the effect of removal processes. For such pollutants, air quality models provide the only practical means available to examine potential emissions reduction impacts on pollutant distributions before actually applying any controls. In this way, an understanding of the atmosphere's chemistry and meteorology is combined with estimates of source emissions to predict possible control strategy effects. Air quality models are also an important tool in gaining understanding about the behavior of various compounds in the atmosphere, such as the reactivity of VOCs.

Air quality models simulate the atmosphere by mathematically representing emissions; initial and boundary concentrations of chemical species; the chemical reactions of the emitted species and of their products; and the local meteorology such as sunlight, wind, and temperature. The models vary greatly in complexity, and thus in the amount of input data and computational resources they require. A number of processes can be parameterized in air quality models, including the inventory of emissions from all sources, gas and aqueous phase chemistry, transport, mixing, deposition, and scavenging. Local conditions such as terrain and cloud cover may also be simulated. The chemistry, transport, and deposition of the compounds are discretized using an equation such as the advection-dispersion reaction equation shown in equation 5 (1):

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (Uc_i) = \nabla \cdot (K\nabla c_i) + S_i[t] + R_i[c_1, c_2, \dots, c_n; T, t] \quad (5)$$

Here,  $\partial c_i / \partial t$  is the change in concentration  $c$  of species  $i$  with time  $t$ ,  $Uc_i$  represents advection,  $K\nabla c_i$  represents turbulent diffusion,  $S_i$  represents emissions (sources) of compound  $i$ , and  $R_i$  is the chemical reactions for species  $c_1$  through  $c_n$  for time  $t$  and

temperature  $T$ . Deposition is represented through advection out of the cell.

To date, model simulations of ozone formation and VOC reactivity studies have been performed using two types of tropospheric air quality models—single-cell Lagrangian models and three-dimensional Eulerian models. Table 3 lists examples of such models.

The single-cell Lagrangian models, often called trajectory or box models, represent the polluted atmosphere by a discrete air parcel that moves over the air basin and receives emissions, which then react in a single well-mixed parcel. Although single-cell models oversimplify transport and diffusion and provide limited information on spatial variability, they can represent chemical transformations in as great detail as is known. Additionally, because of their low input data and computational requirements, single-cell models are practical for performing the large number of simulations required for formal sensitivity analysis. Although these models cannot represent any particular pollution episode with great detail, and have significant uncertainties in their representation of chemistry, an appropriate set of single-cell model scenarios is effective for assessing VOC reactivity under a wide range of conditions. For this reason, the reactivity scale specified by the California Air Resources Board (CARB) in the California Low Emission Vehicles and Clean Fuels (CA LEV/CF) Regulations (24) was developed using a single-cell model (see subsequent discussion). To test how well the scales predict reactivity in a specific airshed, and to examine the spatial and temporal aspects of VOC reactivity, the more physically detailed Eulerian models must also be applied. Results of such tests are also discussed in a later section.

Three-dimensional Eulerian models, also called grid or airshed models, divide an air mass into multiple vertical and horizontal cells where the chemical reactions and (where

Table 3. Examples of Air Quality Models

Model	Reference	Description
Empirical Kinetic Modeling Approach (EKMA)	25,26	Lagrangian, single well-mixed cell. Allows for time-varying emissions and inversion height raise.
Urban Airshed Model (UAM)	27,28	Three-dimensional, urban-scale photochemical model. Specified by the EPA for regulatory applications.
Carnegie/California Institute of Technology (CIT)	29,30	Three-dimensional, urban-scale photochemical model.
CALGRID	31,32	Three-dimensional, urban-scale photochemical model.
Regional Oxidant Model (ROM)	33	Three-dimensional, regional-scale photochemical model.
EPA Models-3	34	Three-dimensional, multi-scale photochemical model.

applicable) emissions occur. These models simulate transport, diffusion, or deposition of the pollutants between cells. Grid models provide the most comprehensive representation of any airshed and provide the only means to predict observed pollution levels in real-world pollution episodes, particularly with respect to spatial and temporal variation. However, these models require large quantities of detailed input data and have high computational demands. Some of the most significant limitations of grid models involve the uncertainties in the input data and chemical mechanisms. Grid models are often applied to an airshed where extensive, carefully examined input data are available, such as that from the Southern California Air Quality Study in the Los Angeles air basin (30). Results can then be compared to ambient pollutant observations to evaluate the accuracy of model predictions. Although models are frequently evaluated against observed ozone data, most studies have not directly compared predictions with observations of VOC and  $\text{NO}_x$  concentrations. Because many factors affect ozone, one does not know whether a model that can predict ozone is giving the right answer for the wrong reason. The few studies that have compared VOC and  $\text{NO}_x$  data indicate that grid models underpredict precursor concentrations by significant factors.

Potential pollution control strategies can be examined with grid models by simulating the effects of reducing specific source emissions and then comparing resultant predicted pollution concentrations with those predicted without the source controls, thus potentially saving the huge efforts and costs of applying ineffective emissions control strategies. Compound and source reactivity can be examined with these models by simulating the effects of adding incremental amounts of a

VOC or of a specific source emission to a *base case* emission inventory.

Grid models are used to assess specific pollution scenarios, account for great physical detail, and provide spatial and temporal information on pollutant behavior; single-cell models are used to represent a wide variety of chemical conditions and perform formal sensitivity analysis. Choosing which model type is best suited for a specific application is often based on balancing the need for physical detail with computational limitations. For these reasons, the study of reactivity relies on both single-cell and grid model predictions, and the results can be compared to help assess the reliability of the reactivity predictions. For more information on types of air quality models and model verification, see Reference 2 and the references therein.

### Chemical Mechanisms

The chemical mechanism is the portion of the airshed model that represents the chemical transformations of the pollutants that are emitted or formed in the atmosphere. This is the term  $R_i$  in equation 5. Because this is the portion of the model that represents how  $\text{O}_3$  is formed from the various types of VOCs in the presence of  $\text{NO}_x$ , it is the critical component for predicting VOC reactivity. The mechanism must be able to take all the chemical factors affecting ozone formation appropriately into account if the ozone predictions of the model are to be credible. Table 4 lists the various chemical mechanisms that are currently in use in air quality models and indicates the airshed modeling applications where they are currently used, along with their relative strengths and weaknesses (35–40).

As indicated in Table 4, all the chemical mechanisms currently in use employ various approaches for condensing or simplifying the complex chemical processes that actually occur. This is because several hundred types of organic compounds have been identified in speciated emissions inventories, and the compounds all have differing reaction rates, amounts of NO oxidation caused by the radicals they form, effects on OH radical and  $\text{NO}_x$  levels, and reactivities of their products. Each reaction has a rate constant that can depend on temperature, pressure, or, for photolysis reactions, the intensity and spectrum of incident sunlight. All of these vary with time of day, season, and meteorological conditions. It is not practical for this level of detail to be represented explicitly in airshed modeling systems as currently employed. Even if it were practical, environmental chamber data are available concerning only a small subset of these reactions, and for all others their rate constants (and for more complex systems, the products they form) need to be estimated by extrapolation or analogy from the simpler, more well-studied systems.

For these reasons, increasing the complexity and number of species and reactions in the chemical mechanism may not necessarily increase the reliability of predictions of the airshed models that incorporate them. Chemical mechanisms are discussed further later in this section.

### Environmental Chamber Experiments

Before any chemical mechanism—whether detailed or condensed—is incorporated in an airshed model, it must be demonstrated to predict at least the major features of the VOC- $\text{NO}_x$ -air photooxidation process. The only practical means for doing this is to conduct experiments using an en-

Table 4. Chemical Mechanisms Currently Used in Air Quality Models

Mechanism	Description	Reference
Statewide Air Pollution Research Center 1990 (SAPRC-90)	Explicit for a large number of organics, but uses a lumped representation for reactive products. Designed specifically for reactivity applications. Evaluated primarily against indoor chamber data.	35
Carbon Bond IV (CB4)	Lumped by number of carbon bonds in compounds. Specified by EPA for regulatory purposes. Evaluated against outdoor chamber data.	36
Lurmann, Carter, Coyner (LCC)	Earlier and more condensed version of SAPRC-90. Used for CIT grid model reactivity assessment calculations until recently. Evaluated against chamber data.	37
Regional Acid Deposition Model, version 2 (RADM-2)	Developed for use in regional acid deposition modeling. Similar to LCC in detail, except more detailed model for peroxide formation. Evaluated against chamber data.	38
Harwell Mechanism	Extensively used in Europe. Very large number of compounds represented explicitly. Not evaluated with chamber data.	39
SAPRC-93 Mechanism	Updated version of SAPRC-90, same level of detail. More consistent with recent environmental chamber experiments.	40

vironmental chamber, also called a smog chamber, where the chemical processes of interest are occurring under controlled and well-characterized conditions. It can then be determined whether the experimental results are consistent with the predictions of models using the mechanism. Chemical mechanism development experiments have been performed in indoor chambers of ~3000–5000 L using artificial light sources (41), much larger outdoor chambers (42–44), and with smaller indoor reaction bags (45,46).

Various types of chamber experiments are used to test different aspects of the chemical mechanisms. Irradiations of single VOCs in the presence of  $\text{NO}_x$  and air test the mechanisms for the individual compounds;  $\text{NO}_x$ -air irradiations of more complex VOC mixtures test the performance of the model as a whole (47–50); and experiments where the effect of adding single VOCs or VOC mixtures to irradiations of  $\text{NO}_x$  and complex mixtures test model predictions of incremental reactivity (40,46,51–53). Evaluation of chemical mechanisms with chamber data is complicated by uncertainties in chamber effects (48–50,54) such as deposition to the walls, and separate characterization experiments are needed to evaluate models for these effects. The characterization results are used when evaluating the mechanism of interest (48–50). Although uncertainties are introduced in such evaluations,

the uncertainties in evaluating chemical mechanisms using chamber data are far less than the uncertainties in attempting to evaluate mechanisms by comparing full airshed modeling results with ambient air data. With chamber experiments, the amounts of input pollutants are accurately known, and no uncertainties regarding dilution or transport need to be considered.

Current chamber data are available to test the mechanisms for only a subset of the many types of VOCs emitted into the atmosphere. For the other species, reactions are either derived by analogy with mechanisms for compounds that have been studied, or they are represented in the model as if they reacted in the same way as some other species. The latter is referred to as lumping, where a single species is used in the model to represent an entire class of compounds assumed to react in the same way, or a group of model species is used to represent various aspects of the reactions of various chemical compounds. The various lumping approaches, and the approximations and inaccuracies they introduce, vary depending on the mechanisms (refer to Table 4).

#### QUANTIFICATION OF VOC REACTIVITY

A number of possible methods to quantify the impact of a VOC on ozone formation have been examined. Early reactivity experiments were based on amounts of ozone formed when the VOC is irradiated in the presence of  $\text{NO}_x$  in environmental chambers (eg, 55–57). However, individual VOCs are not emitted in the absence of other reactive organics, so such experiments cannot be expected to represent atmospheric conditions. Furthermore, there are chamber wall and background effects which affect the results of such experiments, particularly if the compound reacts slowly or has radical sinks in its mechanism (48,49,54,58–60). An alternative measure that has been proposed is comparison of the OH radical rate constants between VOCs (61–63). Although not strictly a measure of ozone formation, for most compounds reaction with OH is the main process that initiates the VOC ozone-forming reactions. This approach has the significant advantage that the OH rate constants are known or can be estimated for essentially all VOCs of relevance to most regulatory applications (20,64,65), and the OH rate constants are properties only of the VOC, and not the environment where the VOC is emitted (other than small temperature dependencies.) However, this method does not account for the significant differences in the subsequent reaction pathways of the initial products, which can affect how much ozone is formed after the VOC-OH reaction (22,23).

In particular, model calculations have shown that incremental reactivities of VOCs depend not only on how fast the VOC reacts, but also on the tendency of the VOC to enhance or inhibit radical levels, the tendency of the VOC to remove  $\text{NO}_x$  from the system, and the reactivity of the VOC major products (19,22,66,67). For example, aromatics, which have strong  $\text{NO}_x$  sinks and radical sources in their mechanisms, were found to have relatively high reactivities under low VOC/ $\text{NO}_x$  conditions, but were found to have negative reactivities when the VOC/ $\text{NO}_x$  ratio was sufficiently high. For this reason, the OH radical rate constant has been shown to correlate poorly with other measures of ozone formation potential, particularly for the more rapidly reacting VOCs (68,69).

Because of the limitations of the OH radical rate constant scale (70), it has been argued that a scale based on incremen-

tal reactivities would provide a more comprehensive measure of the effect of a VOC on actual ozone formation (35,69). Incremental reactivity is defined as the change in ozone caused by a change in the emissions of a VOC in a specific air pollution episode. To remove the dependence on the amount of VOC added, incremental reactivity is defined by equation 6 as the limit as the amount of VOC added approaches zero, ie, as the derivative of ozone with respect to VOC (as shown on the lower plots of Fig. 1):

$$IR_i = \frac{\delta[O_3]}{\delta[VOC_i]} \quad (6)$$

Here,  $IR_i$  is the incremental reactivity and the subscript  $i$  denotes the VOC being examined. This reactivity definition takes into account the effects of all aspects of the organic reaction mechanism and the effects of the environment where the VOC is emitted. However, model calculations (23,25,69,71) and environmental chamber experiments (72) have shown that changes in environmental conditions can significantly affect incremental reactivities, both in a relative and in an absolute sense. Therefore, the incremental reactivity is a function of the episode as well as of the VOC. This presents obvious problems in developing reactivity scales for use in VOC control regulations which will be applicable under all conditions. Methods for dealing with this episode dependence are discussed in the subsequent section on variability.

The incremental reactivity of a VOC under true ambient conditions cannot be measured directly—other than by changing emissions and then observing the resulting changes of air quality for enough years to factor out effects of meteorological variability—but can be estimated either by computer model calculations or by suitably designed environmental chamber experiments. Both types of estimation approaches have their limitations. In the case of model calculations, uncertainties and approximations in the model for airshed conditions, in the model formulation, and in the chemical mechanism cause uncertainties in the predicted ozone impacts, as discussed subsequently. In the case of experiments, it is difficult for the conditions of the experiment to simulate ambient conditions, so the results do not have general applicability. For these reasons, modeling and experimental measurements are used in conjunction for examining reactivity.

In an early model simulation, it was shown that, when adding a given amount of a VOC to the other VOC inputs in EKMA model simulations, the calculated change in ozone varied widely among different VOCs at low VOC/NO<sub>x</sub> ratios, but were lower and less variable under high VOC/NO<sub>x</sub> conditions (68). Although the VOC/NO<sub>x</sub> ratio was probably the most important single environmental factor affecting reactivity, other factors are important as well (22). Simulations of environmental chamber experiments resulted in different incremental reactivities (both absolute and relative) than simulations of atmospheric conditions, indicating that incremental reactivities measured in chamber experiments should not be used to assess atmospheric reactivities without the benefit of model calculations to account for the differences between chamber and airshed conditions. In addition, it was shown that the number of days in the pollution episode and the nature of the other VOCs present also had a non-negligible effect on VOC reactivities (22). There was still some variability in relative reactivities among different one-day airshed model scenarios

even after NO<sub>x</sub> inputs in the scenarios were adjusted to yield consistent conditions of NO<sub>x</sub> availability (23).

The factors affecting reactivity from the perspective of the chemical reactions actually responsible for ozone formation have also been investigated (19,66,67,73), showing that the relative contribution of VOCs to the reactions that are directly responsible for ozone can be quite different than the relative incremental reactivities of those VOCs. This is because many VOCs have high (or negative) incremental reactivities—not because of the ozone formed by their own reactions, but because their reactions affect how much ozone is formed from other VOCs. For example, if the reactions of a VOC significantly affect radical levels (as represented by  $\gamma$  in eq. 4), they will affect how much O<sub>3</sub> is formed from the reactions of other VOCs. For many VOCs, this indirect effect on reactivity makes a larger contribution to its incremental reactivity than the ozone formed by the VOC direct reactions (19,66,67). This result has also been shown from an analysis of the results of incremental reactivity experiments carried out under maximum reactivity conditions (52,53).

#### Environmental Chamber Reactivity Assessments

One way to assess VOC reactivity is to measure its effect on ozone when irradiated in the presence of NO<sub>x</sub> and other VOCs in environmental chamber experiments. Although chamber results are not applicable in a general sense for regulatory use, experimental results are necessary to ensure modeling results are realistic. Such studies are underway or have recently been completed at the University of California at Riverside (52,53,72,74), at the General Motors Research Laboratory (GMRL) (45,46), and at the University of North Carolina (UNC) (75). Although the studies have many similarities, the objectives are different. Some studies (41,52,53,72,74) were carried out primarily to evaluate the chemical mechanisms used in airshed models to predict atmospheric reactivity, which as discussed is essential for assuring their reliability. In the first study (52,53) a relatively large number of compounds were studied using a blacklight light source, relatively high NO<sub>x</sub> MIR-like conditions, and a highly simplified mixture to represent other VOCs in the atmosphere. In chamber experiments studying reactivity, the term reactive organic gas (ROG) surrogate is used to refer to this mixture representing the other atmospheric VOCs, whereas the term VOC is used to refer to the individual compound whose reactivity is being studied. In the second study (72), the effects of varying the NO<sub>x</sub> conditions while using a more complex and realistic ROG surrogate was examined. The results were compared with the predictions of both the SAPRC-90 mechanism which was used in the reactivity assessments discussed, and also an updated version of this mechanism designated SAPRC-93 (40). The SAPRC-90 mechanism agreed reasonably well with the experimental results for most VOCs, except for the internal alkenes, where SAPRC-93 performed significantly better. Neither mechanism performed particularly well in simulating reactivity differences among xylene and trimethylbenzene isomers, although this discrepancy has been corrected in newer versions of the SAPRC mechanism which are still under development (76). The mechanisms performed quite well in simulating the effects of varying the NO<sub>x</sub> levels and the nature of the ROG surrogate.

The objective of other experiments (45,46) was primarily to evaluate how well experimental incremental reactivities correlate with the modeled MIR scale. Incremental reactivities of several representative VOCs were measured as a function of amount of VOC added under approximately maximum reactivity conditions. A xenon arc light source (which gives a better approximation to the spectrum of sunlight than blacklights) and relatively small volume reaction bags were employed. Although the ROG surrogate only approximated the average background conditions assumed for modeling the MIR scale, the experimental reactivity results correlated well with the modeled reactivity results. Of note, the chemical mechanism used in the trajectory model was developed from smog chamber results, so some omissions or errors may impact both the chamber and the model reactivity values. The experiments were not intended for mechanism evaluation, although they may be useful for this purpose if additional light characterization experiments are carried out.

A large outdoor environmental chamber was used to compare ozone formation from various complex mixtures designed to closely duplicate components in vehicle exhausts (75), and similar experiments were performed using an indoor environmental chamber to examine the reactivity of actual alternative fuel vehicle exhaust (77). The purpose was both for evaluating chemical mechanisms, and also for direct comparison of ozone formation from chemically realistic mixtures (75). The results of this study were compared with predictions of the CB4 mechanism, and even though very good agreement was found for most simulations, the CB4 was believed to exhibit too large of an increase in ozone production with increasing temperatures over 80°F (26.7°C). The potential reactivity of the exhaust emissions, which agreed reasonably well with current air quality model estimates, was evaluated (77).

Finally, a series of environmental chamber experiments was performed, upon which a proposal was made that reactivity is a conserved property regardless of background VOC composition, and that ozone production is independent of  $\text{NO}_x$  under conditions that are not  $\text{NO}_x$  limited ("light-limited") (78). Based on this hypothesis, a commercial instrument intended to directly measure reactivity in an air stream was developed. This instrument and hypothesis were the focus of some recent evaluation studies (79,80). Results from both studies indicate reasonable to excellent agreement under specific environmental conditions among the instrument, static environmental chamber results, and some chemical mechanism modeling predictions. They also found that, for the conditions studied, incremental reactivity was additive within the experimental uncertainty. However, both studies required major modifications to the instrument before it could be used for reactivity measurements, and the hypothesis that smog formation is independent of  $\text{NO}_x$  in a light-limited regime was not found to be valid.

Although environmental chamber studies are essential for mechanism evaluation and assessments of reactivities of complex mixtures, incremental reactivities in environmental chambers are not the same as incremental reactivities in the atmosphere. It is not practical to duplicate all of the environmental conditions which affect a VOC incremental reactivity in environmental chamber experiments, and even if it were it would not be practical to use them to comprehensively investigate how reactivities vary over the wide variety of conditions that occur in the atmosphere. For this, model calculations are

required. Various modeling approaches to assessing reactivity and developing reactivity scales are discussed in the following sections.

#### Relative Reactivity Scales

A general scale which ranks the reactivities of VOCs would clearly aid the development of regulatory applications which take differences in VOC reactivity into account. However, because incremental reactivities depend on environmental conditions, no incremental reactivity scale will correctly predict relative ozone impacts under all conditions (even if there were no uncertainties in the models, the chemical mechanism, and the airshed conditions). This can be partially accounted for through the use of a relative, rather than absolute, comparison of reactivities. In other words, we do not compare the absolute amount of ozone formed per amount of VOC added, but the amount of ozone formed relative to other VOCs. This concept is applied to sources as well as compounds. For example, if one is comparing the reactivity of emissions from a gasoline-fueled vehicle to that from a compressed natural gas (CNG) vehicle, what is most important is not that the gasoline-fueled exhaust has a reactivity of 1.00 g of ozone per gram of exhaust VOC, and CNG exhaust has a reactivity of 0.20 g of ozone per gram exhaust VOC. These quantities are dependent on location and time. What is of greater interest is that the CNG exhaust is 5 times less reactive, so the CNG vehicle can emit about five times as much VOC in any area and still have a similar impact on ozone levels. Defining reactivity in reference to other reactivity values rather than to absolute ozone formation allows reactivity values to be more readily evaluated and compared. To calculate relative compound reactivities, we quantify the reactivity of individual VOCs as compared to a reference compound or, better, a VOC mixture (ie, the reactivities are normalized). When these normalized compound reactivities are quantified in a relative sense, the set of reactivities is referred to as a relative reactivity scale.

Although the use of a reactivity scale reduces the effect of reactivity variabilities, it cannot completely account for environmental effects. Nevertheless, the only practical alternative to using a general reactivity scale is regulating all compounds as if they were either reactive or unreactive, ie, using an implicit reactivity scale where all compounds have reactivities of either 0 or 1. This method has obvious shortcomings. For these reasons, a number of reactivity scales have been developed, and are summarized in Table 5.

#### Trajectory Model Reactivity Assessments

Eighteen reactivity scales were developed using the SAPRC-90 chemical mechanism in a single-cell trajectory model (23,89). These scales represent the average results from 39 modeled trajectories, each representing an urban area with varying, though low, VOC-to- $\text{NO}_x$  ratios, as shown in Table 6. Averaging reactivities across these trajectories accounts for some of the variability caused by environmental conditions.

The 18 reactivity scales were derived using nine different approaches for dealing with the dependence of reactivity on environmental conditions and on two methods for quantifying ozone impacts. Seven of these scales are summarized in Table 7. However, two important scales, the maximum incremental reactivity (MIR) and maximum ozone incremental reactivity (MOR), are reasonably good representatives of the

Table 5. Summary of Compound Reactivity Modeling Studies

Reference	Model Type	Mechanism	Application
81	Trajectory	Harwell	Two-layer multiday trajectory simulations of reactivity. Referred to as POCP scales.
82	Three-dimensional (CIT)	LCC	Calculation of 3 reactivity scales for 11 lumped compounds. Simulations were performed for a three-day period in the Los Angeles area (the SCAQS episode).
23	Trajectory	SAPRC-90	Development of 18 reactivity scales (including the MIR and MOIR) for 117 compounds. Results are the average of 39 trajectory simulations for 10-hour periods.
83	Trajectory and three-dimensional (CIT)	SAPRC-90	Review of rate constant uncertainties and also portions of (84,85,87). Report.
84	Trajectory	SAPRC-90	Rate constant uncertainty calculations for the reactivities of 26 compounds under MIR- and MOIR-type conditions. One averaged trajectory was used rather than the 39 used in the Carter MIR and MOIR calculations.
85	Three-dimensional (CIT)	SAPRC-90	Calculation of 3 reactivity scales for 27 compounds. Simulations were performed for the SCAQS episode.
86	Trajectory	SAPRC-90	Calculation of the contributions of 18 compounds to ozone concentrations in the Lower Fraser Valley.
87	Three-dimensional (CIT)	SAPRC-90	Rate constant uncertainty calculations for the scales and compounds in the above study (85).
88	Trajectory and three-dimensional	SAPRC-90	Calculation of five compound reactivities under MIR and MOIR conditions.

Table 6. Summary of Initial Basecase Conditions Used in Development of Carter Reactivity Scales<sup>a</sup>

City	VOC/NO <sub>x</sub>	City	VOC/NO <sub>x</sub>	City	VOC/NO <sub>x</sub>
Atlanta, Ga.	7.3	El Paso, Tex.	6.6	Philadelphia, Pa.	6.2
Austin, Tex.	9.3	Hartford, Conn.	8.4	Phoenix, Ariz.	7.6
Baltimore, Md.	5.2	Houston, Tex.	6.1	Portland, Oreg.	6.5
Baton Rouge, La.	6.8	Indianapolis, Ind.	6.6	Richmond, Va.	6.2
Birmingham, Al.	6.9	Jacksonville, Fla.	7.6	Sacramento, Calif.	6.6
Boston, Mass.	6.5	Kansas City, Mo.	7.1	St. Louis, Mo.	6.1
Charlotte, N.C.	7.8	Lake Charles, La.	7.4	Salt Lake City, Utah	8.5
Chicago, Ill.	11.6	Los Angeles, Calif.	7.6	San Antonio, Tex.	3.9
Cincinnati, Ohio	6.4	Louisville, Ky.	5.5	San Diego, Calif.	7.1
Cleveland, Ohio	6.6	Memphis, Tenn.	6.8	San Francisco, Calif.	4.8
Dallas, Tex.	4.7	Miami, Fla.	9.6	Tampa, Fla.	4.4
Denver, Colo.	6.3	Nashville, Tenn.	8.1	Tulsa, Okla.	5.3
Detroit, Mich.	6.8	New York, N.Y.	8.1	Washington, D.C.	5.3

<sup>a</sup> Ref. 23.

full set, and are discussed in more detail below. The MIR scale primarily reflects the effect of the VOC on ozone formation rates. The MOIR, Equal Benefit Incremental Reactivity (EBIR), and the base-case average ratio ozone yield scales are more sensitive to the effect of the VOC on ultimate O<sub>3</sub> yields in NO<sub>x</sub>-limited conditions. Scales based on integrated O<sub>3</sub> are sensitive to both factors, but tend to be more similar to MIR than MOIR (see also the discussion in following sections). Scales sensitive to effects of VOCs on ozone formation rates generally give higher relative reactivities for aromatics, and lower relative reactivities for alkanes, than those based on ultimate O<sub>3</sub> yields in NO<sub>x</sub>-limited conditions.

Two of the above scales which have been most seriously considered for regulatory use are the MOIR scale and the MIR scale. The MOIR is based on incremental reactivities for NO<sub>x</sub> conditions which are most favorable to ozone formation, as indicated by the "MOR" point on the bottom-left plot in Figure 1.

The MIR is based on the incremental reactivities of VOCs under relatively high NO<sub>x</sub> conditions where the VOCs have their highest incremental reactivity, as is also shown on the bottom-left plot of Figure 1.

Use of the MIR scale has been proposed for regulatory applications because the MIR scale reflects reactivities under environmental conditions which are most sensitive to effects of VOC controls (22,23,70). The MIR scale may be less accurate than others in predicting O<sub>3</sub> effects under lower NO<sub>x</sub> conditions; however, because of the lower sensitivity of O<sub>3</sub> under those conditions, the practical impact of those inaccuracies is less important than would be the case under the conditions where the scale is designed to apply. The MIR scale was also found to correlate well to scales based on integrated O<sub>3</sub> yields, even in lower NO<sub>x</sub> scenarios. Nevertheless, the MOIR scale is attractive because it is more representative of the worst case ozone formation conditions in various airsheds, and

Table 7. Summary of Major Characteristics of Carter Reactivity Scales<sup>a,b</sup>

Scale	Type of Scenarios Used	Derivation of Scale from Individual Scenario Reactivities	Ozone Quantification	Reflects Effect of VOC on:
Maximum incremental reactivity (MIR)	Low ROG/NO <sub>x</sub> conditions where O <sub>3</sub> is most sensitive to VOC changes	Averages of incremental reactivities in the MIR scenarios	Maximum ozone	Ozone formation rates
Maximum ozone incremental reactivity (MOIR) <sup>b</sup>	Moderate ROG/NO <sub>x</sub> conditions where highest O <sub>3</sub> yields are formed	Averages of incremental reactivities in the MOIR scenarios	Maximum ozone	Ultimate ozone yield
Equal benefit incremental reactivity (EBIR)	Higher ROG/NO <sub>x</sub> conditions where VOC and NO <sub>x</sub> control are equally effective in reducing O <sub>3</sub>	Averages of incremental reactivities in the EBIR scenarios	Maximum ozone	Ultimate ozone yield
Base-case average ratio: O <sub>3</sub> yield	Base-case conditions: ROG/NO <sub>x</sub> conditions are as observed for the individual scenarios	Averages of incremental reactivities in the base case scenarios	Maximum ozone	Ultimate ozone yield
Base-case least squares error: O <sub>3</sub> yield	Base case	Minimizes the sum of squares change in ozone which would occur if a "null test" substitution were made in all the scenarios based on the scale <sup>c</sup>	Maximum ozone	Depends on the variability of scenario conditions <sup>d</sup>
Base-case average ratio: integrated O <sub>3</sub>	Base case	Averages of incremental reactivities in the base-case scenarios	Integrated ozone	Ultimate ozone yield
Base-case least-squares error: integrated O <sub>3</sub>	Base case	Same as base-case least-squares error: O <sub>3</sub> yield <sup>c</sup>	Integrated ozone	Ultimate ozone yield

<sup>a</sup> Ref. 23.<sup>b</sup> The MOIR scale is also referred to as the Maximum Ozone Reactivity (MOR) scale.<sup>c</sup> A "null test" substitution based on a reactivity scale consists of substituting VOC emissions such that the scale predicts there would be no change in ozone. Two types of least-squares error scales were derived—one based on substitution of the individual VOCs for the base ROG mixture, and one on substituting the base ROG for the VOCs. The scales are similar except for VOCs with variable incremental reactivities distributed around zero.<sup>d</sup> Depends on effect on O<sub>3</sub> formation rate if scenarios are highly varied in ROG/NO<sub>x</sub> conditions (47,69,90), but depends more on effect on ultimate O<sub>3</sub> yield if the ROG/NO<sub>x</sub> conditions are more narrowly distributed, as with the EPA scenarios (91) used in the most recent reactivity scale derivation (23,89).

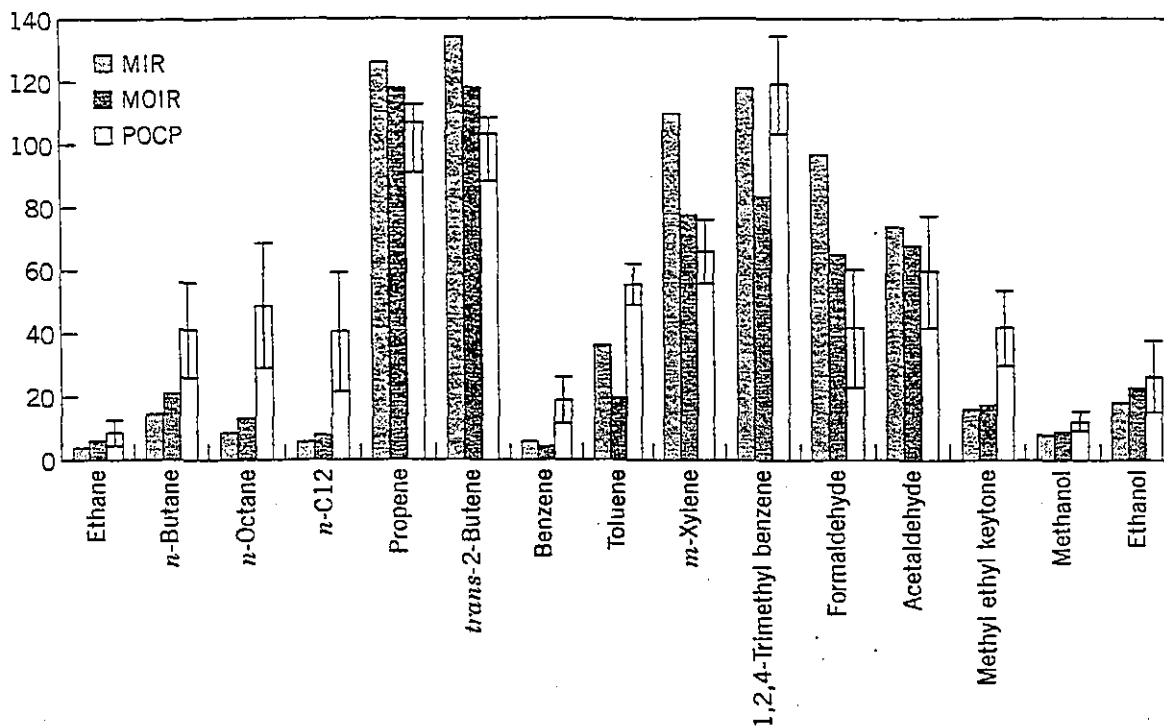
also because it tends to be more conservative in predicting substitution benefits for most alternative fuels. The MIR scale tends to predict larger reactivity benefits for slowly reacting compounds than may be appropriate, because the higher NO<sub>x</sub> levels of MIR scenarios cause suppressed radical levels, which decrease the amount that slower reacting compounds react in the scenarios. Ultimately, in the first reactivity-based regulatory action, CARB concluded that the MIR was a superior method to the OH scale for assessing reactivity and used the scale as a basis for deriving reactivity adjustment factors (RAFTs) in California's LEV/CF regulations (92). RAFTs are discussed further later in this article. The MIR scale is now also widely used as a means for comparing reactivities of vehicle emissions during various driving cycles as well as for evaluating the use of alternative fuels (93).

An alternative approach that may have the best features of both the MIR and MOIR would be to use a scale based on integrated ozone under base-case or maximum ozone conditions. This has the advantage of the MIR scale in that it performs well in predicting reactivity effects under high NO<sub>x</sub> conditions that are most sensitive to VOCs (because it correlates reasonably well to MIR for most VOCs), while also being based on conditions of scenarios that are more representative of worst-case O<sub>3</sub> pollution episodes. Furthermore, in the context of Eulerian model simulations where ozone impacts vary with

both time and space, integrated ozone throughout the full air basin and time period of the episode is arguably a more robust measure of the exposure of the environment to ozone than the peak ozone concentration, which might be highly localized in time and place. Comparisons of Eulerian model predictions with the MIR and MOIR scales are discussed subsequently.

An alternative series of reactivity scales derived using a trajectory model are the photochemical ozone creation potential (POCP) scales, also shown on Table 5, which were calculated by Derwent and other researchers in Europe (81,94) using the Harwell mechanism (39) and a two-layer Lagrangian model representing various multiday trajectories across Europe. The reactivities are calculated from the change in mid-afternoon ozone for each day in the trajectory resulting from removing the test VOC from the emissions, divided by the integrated emissions of the test VOC up to the time of the ozone observation. Most of the POCP scenarios probably represent low NO<sub>x</sub> conditions.

A comparison of MIR, MOIR, and POCP reactivities for selected VOCs is shown on Figure 3. The MIR and MOIR scales give very similar relative reactivities for most compounds, and are consistent in predictions of which compounds are highly reactive and which are not. However, for reasons discussed previously, the MOIR scale gives lower relative reactivities for aromatics, and also predicts lower relative reactivities for



**Figure 3.** Comparison of MIR, MOIR, and POCP relative reactivities. Incremental reactivities (ozone per gram) are shown relative to ethene = 100. MIR and MOIR reactivities are from (23). POCP reactivities are averages for various trajectories calculated (81), with error bars being the standard deviation of the averages.

radical initiators such as formaldehyde, which have larger effects on rates of ozone formation than on ultimate ozone yields. The MIR, MOIR, and POCP relative reactivities generally predict similar orderings of reactivities (relative reactivities), but some significant differences are observed. The largest differences, particularly for the alkanes and methyl ethyl ketone (MEK) are probably due primarily to differences in the chemical mechanisms employed, rather than the types of scenarios employed. The Harwell mechanism (39) is chemically detailed and intended to be explicit, but, unlike the SAPRC and carbon bond mechanisms, has not been evaluated against chamber data and may not adequately represent the large  $\text{NO}_x$  sink processes in the aromatic photooxidations that give them low or negative reactivities under low  $\text{NO}_x$  conditions. The relatively low reactivity predictions for the higher alkanes by the SAPRC-90 mechanism has been verified by environmental chamber experiments (40,52,53,72). Effects of differences and uncertainties in chemical mechanisms on reactivity scales are discussed in more detail in a later section.

A different trajectory model was also used to evaluate reactivity (86). This study used the SAPRC-90 chemical mechanism in the ozone isopleth plotting research version (OZIPR) trajectory model (95) to predict the reactivity of 17 VOCs and methane in the Lower Fraser Valley of Canada. This study designated nine VOCs as significant contributors to the ozone concentrations, seven of which represent lumped compound groups. The greatest contributor to ozone formation was found

to be ARO2, a lumped model species used to represent the xylenes and other fast reacting aromatics.

#### Eulerian Model Reactivity Assessments

A serious concern about the regulatory application of scales such as MIR and MOIR is that they are all based on the single cell (Lagrangian) model simulations of single-day pollution episodes. MIRs have been developed based on 10-h simulations, whereas some organic compounds may remain in an urban airshed for 2–3 days. The trajectory model lacks the physical detail, the spatial and temporal detail of emissions and resulting pollutants, and the multiday pollution effects that can be represented in Eulerian models. For that reason, it is important that the scales derived using trajectory models be evaluated using more detailed models. Three sets of such studies have been carried out to date (82,85,87,88).

All three studies employed the Carnegie/California Institute of Technology (CIT) Model (29,30) applied to a three-day air pollution episode in the Los Angeles air basin (30). In addition, one study (88) also applied the CIT model to the Swiss Plateau to study the use of reactivity over regional domains that are less  $\text{NO}_x$ -rich. A challenge in comparing VOC reactivity using results between box and grid modeling studies is the difference between quantification measures, or metrics, that can be defined from each analysis method. Differences in the spatial and temporal representation of emissions can

also make the comparison of results difficult. In the Eulerian reactivity studies, incremental emissions of the test compound were modeled by increasing the test VOC proportionally to the spatial and temporal distribution of the base organic species emissions. The rates of all organic species emissions in each modeling cell for each hour were used to determine the rate of the test species emission in that cell. This is represented mathematically by equation 7, where, at time  $t$  in model cell  $x, y, z$ , the perturbed emission ( $E_i^p$ ) of test species  $i$  is calculated as the base emission of that species ( $E_i^b$ ) plus a fraction, ( $\alpha$ ), of the sum of the total base level emissions of reactive organic gases. Index  $j$  refers to each represented explicit or lumped emitted VOC. This modeling method accounts for the effect of emissions variation, transport, and multiday reactions.

$$E_i^p(x, y, z, t) = E_i^b(x, y, z, t) + \alpha \sum_j E_j^b(x, y, z, t) \quad (7)$$

In addition to different representation of emissions by trajectory and three-dimensional models, results from three-dimensional modeling can be described in a number of ways. Three of the most useful metrics are the difference between peak ozone concentrations predicted using the base and perturbed inventories, and population- and exposure-weighted exposure to ozone levels exceeding a threshold value (82,85). Eulerian model results can also be compared across different parts of the modeled domain, which have varying VOC to  $\text{NO}_x$  ratios because of pollutant emissions and transport, as well as variation in incident radiation caused by cloud cover (85).

The CIT air quality model has been used with a relatively highly lumped chemical mechanism, the Lurmann, Carter, Coyner mechanism (LCC) (37), to quantify the reactivity of 11 individual and lumped VOCs. This study allowed comparison with single-cell model reactivity studies by others, and also between different metrics of ozone impact, including how the species impact the peak ozone as well as ozone exposure. The results showed that the MIR reactivities did not perform well in predicting peak ozone sensitivities for the model species, but performed reasonably well in predicting effects of model species on integrated ozone exposures over the air quality standard. The MOIR scale did not compare as well as MIR to airshed model derived results for either the impacts on peak ozone or on ozone exposures over the air quality standard. The comparisons (82) are complicated somewhat by the fact that the study utilized the LCC chemical mechanism, which does not correspond directly with SAPRC-90 mechanism species used in calculating the MIR and MOIR scales. However, agreement between the MIR scale and the ozone exposure predictions (82) is remarkably good considering the difference in the mechanisms, models, and ozone impact quantification techniques employed. It was noted in this study that much of the variability found could be ascribed to using a single species (CO in this case) for normalization, which is subsequently discussed.

Subsequent to this study (82), the SAPRC-90 mechanism was implemented in the CIT model (referred to as the CIT-S90) for more direct comparison with the MIR and MOIR reactivity scales (85,87). Here, reactivities are normalized to a mixture of VOCs representative of exhaust emissions, as in other reactivity studies (23,84). Some differences were found which are believed to be due to multiday pollutant carryover and cloud cover represented in the CIT model, which are not accounted for by box models. The CIT-S90 was also used to investigate effects of environmental variabilities and of chemical mechanism un-

certainties on reactivities (discussed in the variability and uncertainty sections, respectively). A more detailed comparison of the CIT-S90 study results and the MIR and MOIR are also presented in later sections.

One other three-dimensional model study of reactivity (88) involved VOC solvents having a wide range of reactivities. The solvents studied included *m*-xylene (the most reactive), parachlorobenzotrifluoride (PCBTf, the least reactive halogenated aromatic), benzotrifluoride (BTF), acetone, ethanol, and isobutane. The CIT-S90 was used for this study. Rate constants of similarly reacting compounds were assumed for those solvents for which chamber studies have not been performed. These compounds not only have a wide range of reactivities, but represent a number of different types of VOCs. Using a box model to quantify the MIR and MOIR reactivities, as seen in Figure 4, a very good agreement was found between the normalized MIR and MOIR reactivities (the reactivities were normalized to the geometric average of the compound reactivities), even though the absolute reactivities differed by a factor of two. These results, along with others (23,85,87,96), suggest that the differences between the reactivity scales (and hence, the impact of differing levels of VOC), are primarily in the absolute magnitude, not the relative amount of ozone formed between different compounds.

## VARIABILITY IN REACTIVITY SCALES

### Variability with Environmental Conditions

One of the stronger debates on the use of reactivity quantification for determining the potential impact of VOCs on ozone is that the absolute amount of ozone formed from a given quantity of VOC is heavily dependent on the local ambient conditions, including the meteorology (wind speed, temperature, mixing height, and humidity), pollutant transport (the residence time of emissions in an urban area), distribution of emissions sources (eg, proportion of biogenic, mobile source, and other emissions), and background pollutant concentrations (eg, the VOC/ $\text{NO}_x$  ratio and the absolute levels

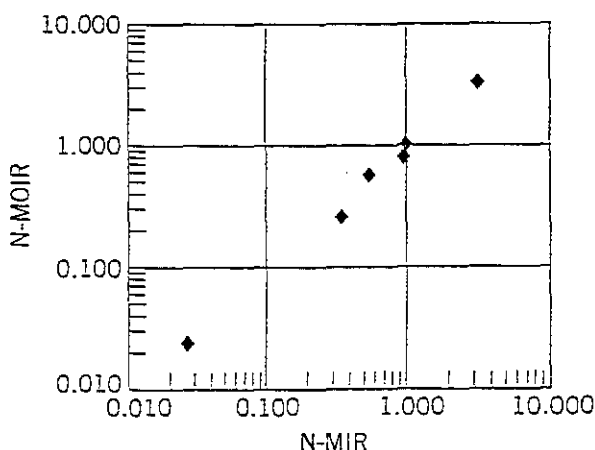


Figure 4. Relative (normalized) N-MIR and N-MOIR reactivities for six solvents (88). In order of increasing reactivity, they are: PCBTf, BTF, acetone, ethanol, isobutane, and *m*-xylene. It is evident that the two scales are nearly linearly correlated for these compounds.

of VOCs and  $\text{NO}_x$ ). This dependence on variable conditions was discussed when presenting various reactivity scales and experimental results.

One effect of variable conditions is that, in the extreme, a compound can go from being fairly reactive under certain conditions to having a negative reactivity under others (eg, toluene). This dependence may make the use of generalized reactivity weighting and the development of reactivity-based control strategies problematic. However, one should also recognize that for most of the organics, those that are highly reactive relative to the other VOCs under one set of conditions remain highly reactive under other conditions. Likewise, the less reactive VOCs remain less reactive. Compounds that vary widely, such as toluene, are the exception rather than the rule. As discussed, this variation is partially accounted for by the use of normalizing and relative ranking in the reactivity quantification of VOCs.

A second issue in the analysis of variability in reactivity with environmental conditions is the effect of  $\text{NO}_x$  and VOC background concentrations. The MIR scale was derived using conditions relatively high in  $\text{NO}_x$ , as might be experienced in areas with a high density of  $\text{NO}_x$  emissions (eg, areas highly impacted by traffic or local industries with significant combustion sources). MOIR conditions occur at lower  $\text{NO}_x$  levels, but the  $\text{ROG}/\text{NO}_x$  ratios are still lower than what might be found in rural areas. Reactivity simulation conditions used by Derwent and Jenkin (81) have even less  $\text{NO}_x$ , which represents conditions where VOC controls and reactivity weighting are relatively ineffective. So the question arises as to how well a measure of reactivity quantification can represent many areas, given the possible range of environmental conditions under which ozone formation occurs. This was, in part, addressed when comparing the MIR, MOIR, and POCF scales, and is addressed further subsequently.

The impact of environmental conditions on reactivity should be discussed at two levels: first, how it affects the reactivity of individual VOCs; and second, how it would likely affect the reactivity of emissions from a source whose composition is made up of a large number of VOCs. As suggested, the absolute amount of ozone formed from any VOC is highly dependent on the environmental conditions. In an area already rich in VOCs (ie, a  $\text{NO}_x$ -limited regime), the small addition of an individual VOC has a lower impact than if that same increment of VOC emissions occurs in an area rich in  $\text{NO}_x$  (where ozone formation is VOC limited). As shown by Carter (23), the average absolute reactivity of a suite of VOCs using the MIR scale is about twice that when using the MOIR scale. Further, there are those few compounds that can go from having relatively high reactivities to low or negative reactivities. This would appear to inhibit the use of reactivity weighting in regulatory applications.

An interesting exercise that addresses the impact of environmental variabilities is a comparison between trajectory model results and three-dimensional model results. By their nature, the three-dimensional models cover domains with a wide range of environmental conditions, going from  $\text{NO}_x$ -rich conditions in urban centers to VOC-rich conditions downwind. Further, they can follow the transport of pollutants over long distances. In two of the modeling studies described previously (85,87), the spatially and temporally resolved ozone impacts were used to calculate impacts on the peak ozone, the potential population-weighted ozone exposure, and the spatial-weighted ozone exposure. From those calculations, the corresponding

compound reactivities were quantified and normalized to the reactivity of a mixture of VOCs (so the results are relative reactivities). As shown in Figure 5, the results from the MIR and MOIR box model calculations (23), conducted for 39 cities (as shown in Table 5), agreed well with related metric results from the airshed calculations for the Los Angeles, CA area.

In interpreting the results of the comparison between the two modeling approaches, and the differences found between the three metrics defined for the airshed model results, it is important to understand the ozone and population patterns in the region. The peak ozone is found in the eastern basin, in an area with relatively little  $\text{NO}_x$ , and thus has a high  $\text{VOC}/\text{NO}_x$  ratio. On the other hand, the population is concentrated more in the western basin, in areas with more dense emissions, and in particular  $\text{NO}_x$ -rich mobile source emissions, and thus having a low  $\text{VOC}/\text{NO}_x$  ratio. Also, the peak ozone is found downwind of the urban area, after the pollutants have had a chance to age, again in contrast to the more densely populated regions which experience fresh emissions. Further, the meteorology (eg, temperatures and mixing heights) in the two portions of the basin are different. Because of these differences, contrasting the population-weighted ozone impact with the peak ozone impact can help capture the level of difference found from environmental variability. The spatial-exposure metric is expected to give results with characteristics of each of the other two metrics.

As shown in Figure 5, the airshed model-derived spatial and population-density weighted results behave similarly to MIRs. The greatest differences are found for formaldehyde and other compounds whose reactivities are highly dependent on photolytic reactions. This may be explained by the use of a reduced photolysis rate in the airshed modeling to account for the observed cloud cover. The box model used clear sky conditions. The reductions in the reactivities are consistent with the sensitivity to the rate constants for the photolytic reactions (84), as addressed in the uncertainty section. In general, airshed model results for Los Angeles agree well with MIRs, and further show that individual organics have very different ozone impacts. Such a study has not been conducted for other regions.

To further compare the trajectory and airshed model results, regression analysis was performed between the box model reactivities and the airshed reactivities. As shown in Table 8, the MIR scale corresponded well with the population exposure-based reactivities, and the MOIR scale agreed well with the CIT-S90 peak-ozone sensitivity. In these two cases, the slope of the regression line is virtually 1 (showing little bias as reactivities increase), and the correlation is high. The CIT-S90 spatial exposure metric correlates well with both the MIR and MOIR scales, but shows some bias in the comparison with the MOIR scale, indicating that the spatial exposure metric finds the less-reactive compounds to be relatively more reactive than does the MOIR scale.

As seen from Figure 5, there are significant similarities between the CIT-S90 metrics as well, although some differences are evident. Differences were quantified by calculating the normalized bias (a value of 1 would indicate a 100% bias) and standard deviation between the scales (Table 9). These differences between potential metrics for reactivity quantification within a modeling study also introduces variability.

A similar issue in regards to the role that environmental variability plays in reactivity quantification is how various meteorological characteristics can affect reactivities.

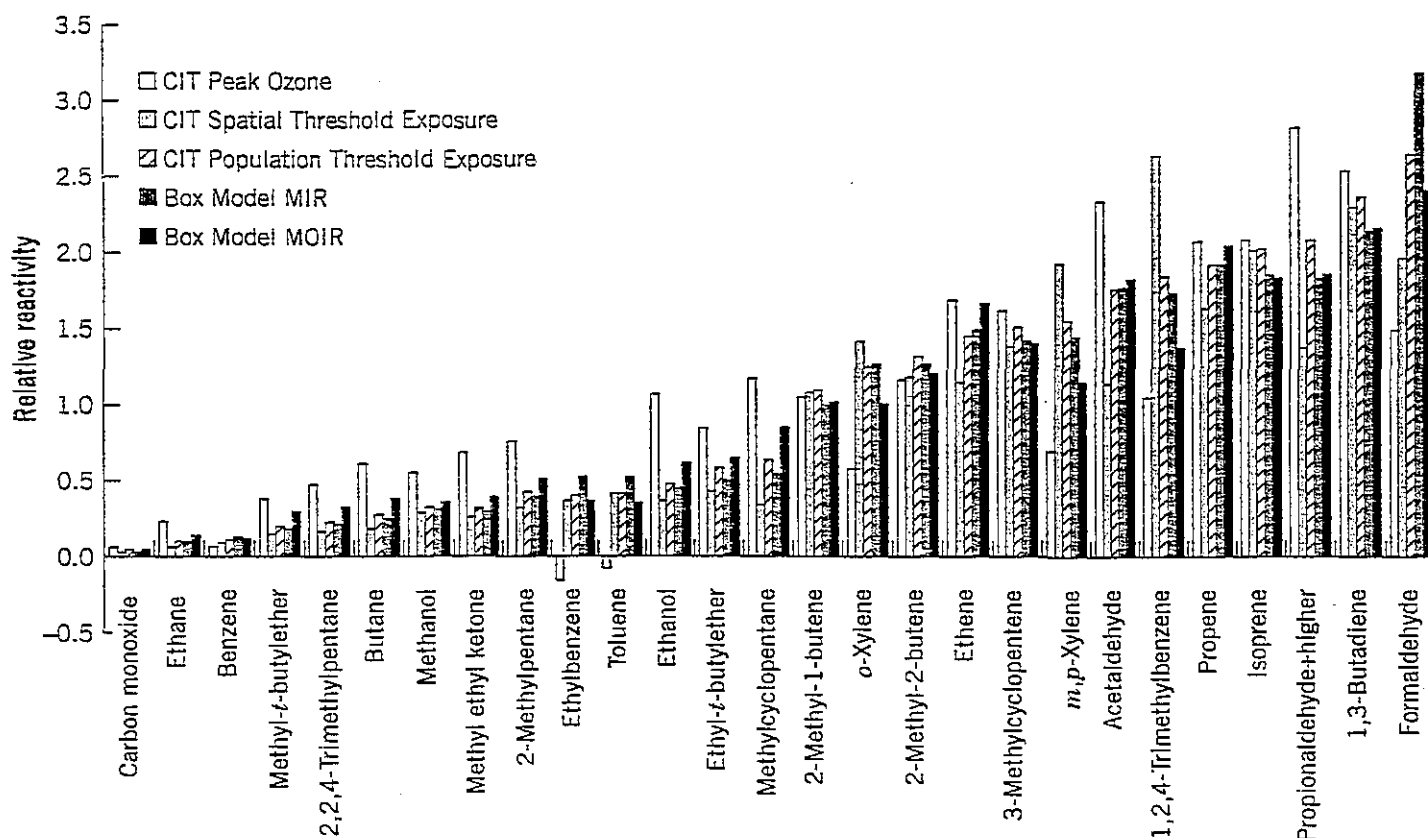


Figure 5. Comparison of three-dimensional and trajectory modeled relative reactivities.

Table 8. Regression Results for Airshed Model Exposure versus MIR and Airshed Peak Ozone versus MOIR Measures <sup>a</sup>

Comparison	R <sup>2</sup>	Slope	Intercept
Population exposure to MIR	0.81	0.88	0.04
Spatial exposure to MIR	0.97	0.98	0.04
Peak to MOIR	0.80	1.01	0.05
Spatial exposure to MOIR	0.96	1.09	-0.06
MIR to MOIR	0.94	1.09	-0.08

<sup>a</sup> Refs. 85 and 87.

Table 9. Normalized Bias and Standard Deviation among Reactivity Metrics Calculated using the CIT-S90 Airshed Model<sup>a</sup>

Comparison	Bias	Standard
Population to spatial exposure	-0.21	0.22
Peak ozone to spatial exposure	0.22	0.52
Peak ozone to population exposure	0.39	0.67

<sup>a</sup> Refs. 85 and 87.

Russell et al. (96) studied the variability in reactivities as found using the results of the box model of Carter under differing conditions, a similar box model (84), and a three-dimensional model (85). First, using just the results of the box model calculations (23), they quantified the inter-city variability

in the absolute species reactivities along the 39 trajectories, and the inter-city variability in the relative reactivities of the individual VOCs along those same trajectories. Normalized MIRs were calculated by dividing each species city-specific MIRs by the geometric mean reactivity of all the species reactivities for that city, and multiplying by the geometric mean reactivity of the 39-city average MIRs. This alleviates the problem that VOCs are generally less reactive, in an absolute sense, in one city versus another. A sample of their results is given in Table 10. As seen, the variability in the reactivity is significantly reduced between the different trajectories when the relative reactivities are used.

Use of relative reactivity generally reduced variability by almost a factor of two, from about 20 to 12%.

#### Impact on Source Reactivity Assessment

The previous discussion pertains to the variability in individual compound reactivity due to changing environmental conditions. In summary, it was found that while the absolute reactivities do vary with environmental differences, the relative reactivities vary much less, although differences are still found. However, regulatory use of reactivity quantification applies to sources, most of which have emissions not of a single VOC but of a mixture of VOCs. For example, automobile exhaust is made up of a myriad of different compounds. Table 11 presents a summary of modeling studies that examine the

Table 10. Example MIRs and Variations among Locations (Mean and Standard Deviation)\*

Compound	Mean Reactivities across 39 Cities (Non-normalized/Normalized)	Standard Deviation (Non-normalized/Normalized)
HCHO	7.2/7.1	1.0/0.58
Methanol	0.56/0.55	0.11/0.064
Ethane	0.25/0.24	0.070/0.045
Toluene	2.7/2.7	0.52/0.28
Pentene	6.2/6.1	1.2/0.64

\* Ref. 96.

Table 11. Summary of Source Emissions Reactivity Modeling Studies

Reference	Model Type	Mechanism	Application
97	Calculated (not modeled)	EPA smog chamber data	Estimated major source reactivities for metropolitan Los Angeles.
98	Trajectory	LCC	Methanol fuel vehicle impacts with respect to conventionally fueled vehicles.
99	Three-dimensional (CIT)	LCC	Potential methanol fuel vehicle impacts for the SCAQS episode (compared to equal mass emissions from conventional vehicles).
100	Three-dimensional (CIT)	LCC	Calculations of RAFs for 4 fuels. Simulations were performed for the SCAQS episode.
101,102	Trajectory	SAPRC-90	Rate constant and exhaust composition uncertainty calculations for the RAFs from reformulated gasolines and methanol.
103	Trajectory and three-dimensional (CIT)	SAPRC-90	Report on box model study described (101,102) and a 3D study of the effects of rate constant and product yield uncertainties on predicted ozone impacts of 5 alternative fuel RAFs.
96	Trajectory and three-dimensional (CIT)	SAPRC-90	Evaluation of combined results of most previous studies (82,84,85,100,101,103). An economic analysis was also performed.
104	Three-dimensional (UAM)	CB4	Modeling of potential impacts of the use of three alternative fuels (CNG, M85, and RFG) in two urban areas. Report.

reactivity of source emissions. An important question is how does environmental variability impact the relative reactivity of source emissions. This issue has been explored in most detail for automotive exhaust emissions, in large part because of the alternative fuel regulations promulgated in California.

In 1990, CARB adopted the LEV/CF regulations (24,92), which are applicable to light- and medium-duty vehicles. The regulations are fuel neutral in that all alternative fuel vehicles (AFVs) can compete in the marketplace as long as they meet exhaust emission standards equivalent or lower in ozone forming potential as those set for vehicles fueled with conventional gasoline. Manufacturers who build automobiles powered by alternative fuels, including reformulated gasoline, can take advantage of the lower ozone-forming potential of these vehicles through the use of RAFs. An RAF, as shown by equation 8, is defined as the ratio of the exhaust reactivity (per gram) of an AFV to that of a comparable conventionally fueled vehicle (CFV). The mass emission rates of NMOG (nonmethane organic gas) exhaust for each AFV is adjusted by the RAF before comparison with the emission standards. In this way, AFVs are allowed to have a higher mass of NMOG emissions than CFVs, so long as the ozone-forming potential of the AFV is no greater than a CFV that just meets the standards. These regulations arose from interest in the use of reformulated gasoline and alternative fuels as a measure to reduce ozone in urban areas.

$$\text{RAF} = \frac{\sum_{i=1}^N F_{A_i} R_i}{\sum_{i=1}^N F_{B_i} R_i} \quad (8)$$

where  $F_{A_i}$  is mass fraction of compound  $i$  in the test fuel exhaust (alternative fuel),  $F_{B_i}$  is mass fraction of compound  $i$  in the base fuel exhaust (conventional gasoline),  $R_i$  is reactivity of species  $i$  (grams ozone formed per gram compound  $i$  emitted), and  $N$  is the maximum number of organic compounds in either fuel A or fuel B.

An RAF is the amount of ozone formed from a unit mass emission from an AFV compared to the amount of ozone formed from an equal mass of VOC emitted by a CFV. Without this type of adjustment, a low mass emission rate of highly reactive exhaust would appear preferable to a higher mass emission of a much less reactive set of species. This adjustment also decreases the impact of compound reactivity variabilities on source reactivity quantification, similar to how compound relative reactivities are less variable than absolute reactivities.

The RAF scale used in the California regulations is calculated using the MIR scale, which was developed using a box model and the SAPRC-90 mechanism. For comparison, the RAFs were calculated for five fuels based on both the SAPRC-90 and the LCC mechanism for the MIR and MOIR scales (100). As seen in Table 12, the results are similar between

Table 12. Comparison of Exhaust Reactivity Adjustment Factors<sup>a</sup>

Fuel	MIR		MOIR	
	SAPRC-90	LCC	SAPRC-90	LCC
Base fuel	1.00	1.00	1.00	1.00
M85	0.37	0.36	0.38	0.38
LPG	0.50	0.50	0.59	0.60
CNG	0.18	0.17	0.23	0.21

<sup>a</sup> Ref. 100.

mechanisms and scales, for each fuel. The largest difference is found for liquefied petroleum gas (LPG) exhaust, which is rich in a few particular compounds.

The impact of environmental condition variability on RAFs has also been investigated (96). Here, both the absolute reactivities and the RAFs of exhaust were calculated for vehicles operated on six fuels along each of the 39 trajectories used in developing the MIRs. The results are shown by box plots in Figure 6. The variation in absolute ozone forming potentials across cities is substantial. However, when the reactivities of exhaust from AFVs are normalized by the reactivity of standard gasoline exhaust (ie, the RAF is calculated for each city individually), variation among cities is sharply diminished (Fig. 6b). The important point here is that while the absolute reactivity of the exhaust may vary significantly, the RAF is relatively invariant across the cities. Again, it is the relative ozone impact that is of greatest concern. Such a marked decrease in variation may not be found for source types emitting fewer compounds.

Other questions remain about the use of reactivity weighting in regulatory practice, mainly because of uncertainties in our representation of atmospheric chemistry, emissions composition uncertainties, and how well our current techniques quantify reactivity. The following section addresses these issues.

## UNCERTAINTIES IN REACTIVITY QUANTIFICATION

### Chemical Mechanism Uncertainty

A concern often raised is that the quantification of compound reactivities is clouded by uncertainties in our knowledge of atmospheric chemistry and its representation through chemical mechanisms. Measurement errors in laboratory kinetic and product studies contribute to uncertainty in the chemical mechanisms used to calculate incremental reactivities. Moreover, the reactions of many of the organic compounds emitted into urban atmospheres have never been studied in controlled experiments. Their representation in chemical mechanisms is based on analogy to compounds of similar structure, creating added uncertainty. At issue is whether the uncertainties in the chemistry significantly impact the calculation of the reactivities for organic compounds.

One way to assess the effects of chemical mechanism uncertainty is to compare reactivity predictions using different state-of-the-art mechanisms which incorporate differing assumptions concerning unknown areas of the chemistry and differing condensation approaches. As discussed, the SAPRC-90 mechanism was used for calculation of the MIR, MOIR, and other reactivity scales because of the number of VOCs it can explicitly represent. The RADM-II and LCC mechanisms employ assumptions similar to SAPRC-90 concerning uncertain portions of the aromatics and other mechanisms, and would be expected to give similar reactivities for the species that the condensed mechanisms are designed to represent. However, this may not be the case for the carbon bond IV (CB4) mechanism, which employs differing assumptions concerning some of the uncertainties in the aromatics mechanisms, and uses different methods for treating alkane and alkene reactions (105). In addition, since the time the CB4 and SAPRC-90 mechanisms were developed, there have been significant changes in our understanding of alkene + ozone reactions, new data on aromatics mechanisms, new laboratory data concerning a number of potentially significant reactions, and the development of a large database of new environmental chamber experiments designed explicitly to test VOC reactivity scales

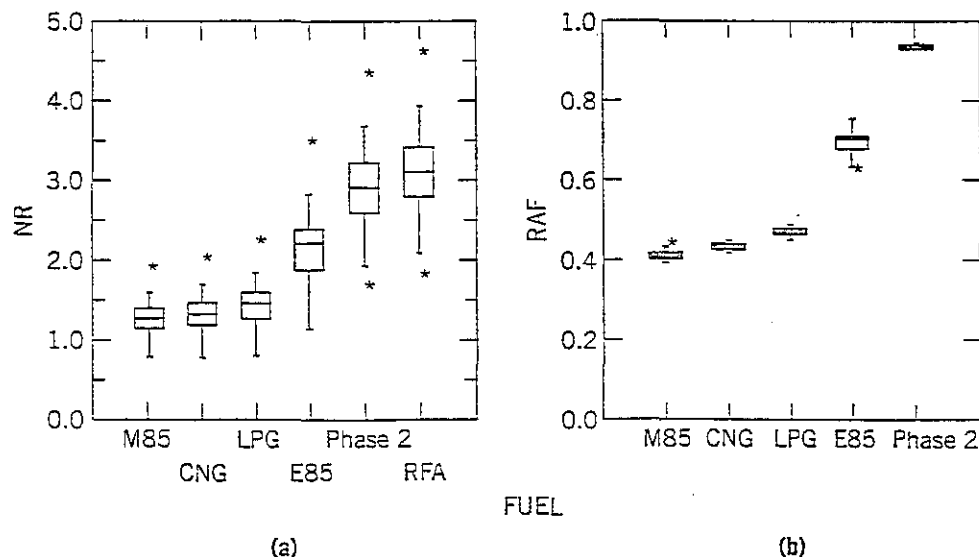


Figure 6. Boxplots of the calculated (a) net reactivities (NRs) and (b) normalized reactivities (RAFTs) across cities (96). The median is represented by a horizontal line. The edges of the boxes represent rough quantiles in the data. Horizontal lines represent the extremes of the data, and outliers are represented by stars.

(41,52,53,60,72). Although the improved SAPRC-93 mechanism (see Table 4) is still under development, a transitional version was used (40) to compare how well the mechanism could simulate results of the previous MIR experiments.

Figure 7 shows a comparison of MIR and MOIR (relative to the standard exhaust) calculated with the SAPRC-90, a recent version of the CB4 (with minor updates concerning peroxy radical reactions which do not significantly affect ozone predictions (106,107)), and the updated SAPRC-93 mechanisms. Other than the mechanism, the scenarios and calculation methodologies are the same (107). The most conspicuous difference is for toluene, for which the developers of the CB4 added a speculative reaction so model simulations could accurately predict the relatively low maximum ozone yields in some toluene-NO<sub>x</sub> outdoor chamber experiments (105). This reaction is not included in the SAPRC-90 mechanism, nor is it in the CB4 mechanism for xylenes. This causes somewhat lower MIR reactivities for toluene and causes toluene to be negatively reactive at the lower NO<sub>x</sub> levels where maximum ozone formation occurs. (The SAPRC-90 mechanism also predicts that toluene becomes negatively reactive at low NO<sub>x</sub> levels, but the NO<sub>x</sub> levels must be much lower than is the case with CB4). In the case of xylenes, where the CB4 lacks this speculative reaction, the MIR and MOIR relative reactivities agree quite well. The somewhat higher CB4 formaldehyde reactivity is believed to be primarily caused by a greater sensitivity of the CB4 mechanism to radical input processes, rather than by differences in the formaldehyde mechanism itself. Except for the internal alkenes, the differences in reactivity predictions between the SAPRC-90 and the SAPRC-93 mechanisms are relatively minor. However, the SAPRC-93 mechanism does not incorporate recent modifications made to the aromatic mechanisms based on results of recent environmental chamber experiments, and other updates to the mechanism are anticipated (76).

More systematic studies of the effects of mechanism uncertainties have been carried out using airshed and box models to explore to what degree uncertainties in chemical rate parameters affect the calculated compound reactivities (84,87,96, 101-103). Monte Carlo analysis has been used with Latin Hypercube Sampling to calculate reactivity uncertainties (84,102). Computational requirements were reduced by using a single set of trajectory conditions that were designed to give results close to the MIRs (23), which were averaged results from the 39 modeled trajectories. Uncertainty estimates were compiled (108) for all rate parameters of the SAPRC mechanism, largely from concurrent reviews of kinetic data (65,109). Results are shown in Figure 8.

Uncertainty estimates (1 $\sigma$ ) range from 30% to 50% of the mean MIR values for most compounds. The estimated uncertainty in the predicted peak ozone concentration for the average MIR simulation conditions was about 30%, relative to a mean prediction of ~0.15 ppm O<sub>3</sub>. For predicted O<sub>3</sub> and MIRs, the most influential uncertainties are those in rate parameters that control the availability of NO<sub>x</sub> and radicals (84). For MIRs, uncertainties in the rate parameters of primary oxidation reactions, or reactions of stable intermediates, are also influential. Uncertainties in many rate parameters have similar effects on the reactivities of various compounds, so the resulting MIRs are strongly correlated. For example, an increase in the photolysis rate for NO<sub>2</sub> increases the reactivity of most species by about the same proportion. Thus, the relative reactivity of one

species compared to another is not affected as much as the absolute MIRs by uncertainties in rate constants (84,102).

For further mechanism evaluation, the box-model rate constant uncertainty studies were extended to a three-dimensional model uncertainty study (87). After the most influential rate parameters had been identified through Monte Carlo simulations (84), those parameters in the CIT-S90 model were varied by twice the estimated uncertainty, and the compound reactivity simulations were then recalculated. Results of one metric studied (spatial exposure) are shown in Figure 9. This analysis, again, found that relative reactivities have relatively low sensitivities to rate constant uncertainties. The implication of this result is further demonstrated by considering uncertainties in source reactivity quantification and RAFs.

### Uncertainties in Emissions Compositions

Emissions composition uncertainties have been cited as a major confounding factor in the use of reactivity weighting for ozone control. To address this issue, the previously described box-model analysis was extended to look at emissions composition uncertainties in addition to mechanism uncertainties. Exhaust emissions from selected fuel/vehicle combinations developed in the Auto/Oil Air Quality Improvement Research Program (AQIRP) (110), were used to calculate RAFs and associated uncertainties (101,102), again using Monte Carlo simulations with Latin Hypercube sampling. Uncertainties in the exhaust compositions were estimated from the variance and covariance of emissions of each compound across the vehicles that the AQIRP study tested on a given fuel. Emissions of each compound were then treated as correlated, normally distributed random variables. Results of RAF uncertainty calculations are shown in Figure 10 for exhaust emissions from prototype flexible and variable-fuel vehicles operated on M85 compared to exhaust emissions from passenger cars operated on industry average gasoline. The mass-based RAF for the AQIRP M85 exhaust composition has a mean value of 0.49 with an uncertainty of 17% (1 $\sigma$  relative to the mean). Compared to the degree of uncertainty in the MIRs for formaldehyde (32%) and methanol (48%), the RAF uncertainty is significantly reduced due to interspecies correlation. This reduction in uncertainty is even more pronounced for RAFs of fuels such as reformulated gasoline that have exhaust compositions closer to that associated with conventional gasoline, as shown in Figure 11.

To further examine the role of variation in emissions composition across fuels, variances of RAFs were calculated using exhaust composition data (92,111,112) for four alternative fuels and standard gasoline. The data consisted of mass fractions of VOC exhaust from transitional low emission vehicles (TLEVS) for each exhaust type, and the mass fraction's associated standard deviation. Variances of the RAFs for each fuel were calculated using the Delta method (113). Each fuel's RAF was calculated as the ratio of two normally distributed random variables. MIR values were calculated based on the average MIR scale. The results are shown in Figure 12, which displays the 5th, mean, and 95th percentiles of each fuel's RAF value. Comparison of Figure 12, which has only one degree of uncertainty, with Figures 10 and 11, suggests that much of the uncertainty comes from the composition. Exhaust emission compositions are derived from a small number of

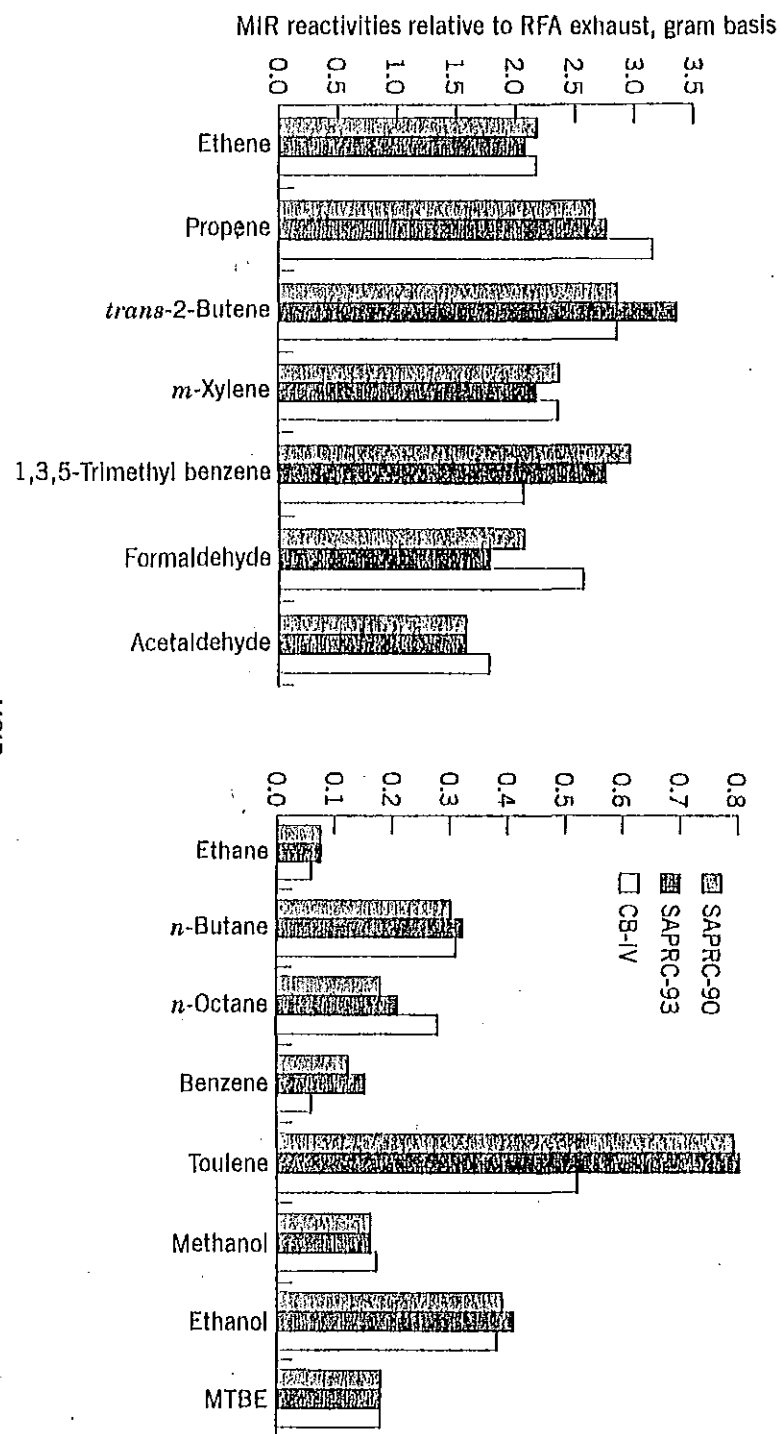
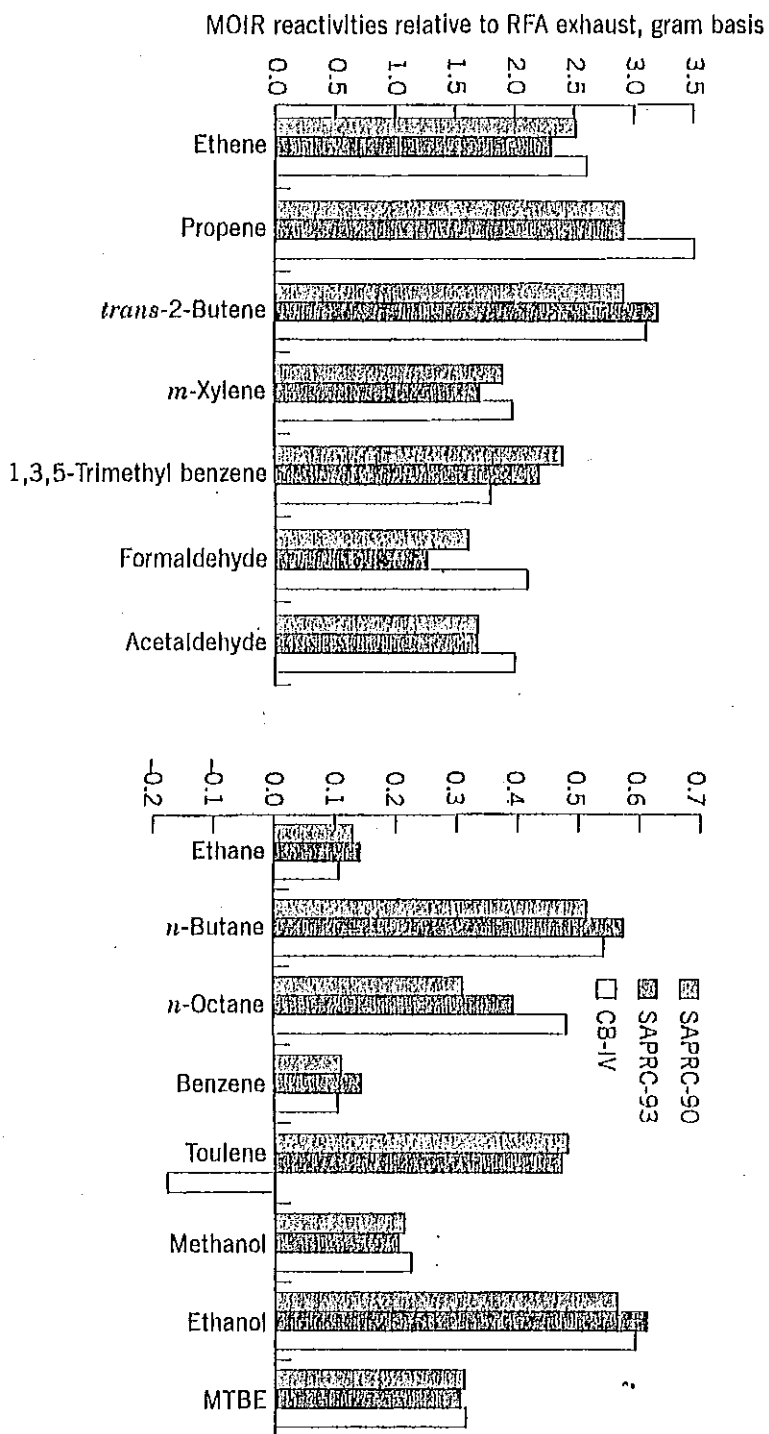


Figure 7. Comparison of incremental reactivities of representative VOCs, relative to standard exhaust, calculated using the SAPRC-90, SAPRC-93, and Carbon Bond IV mechanisms.

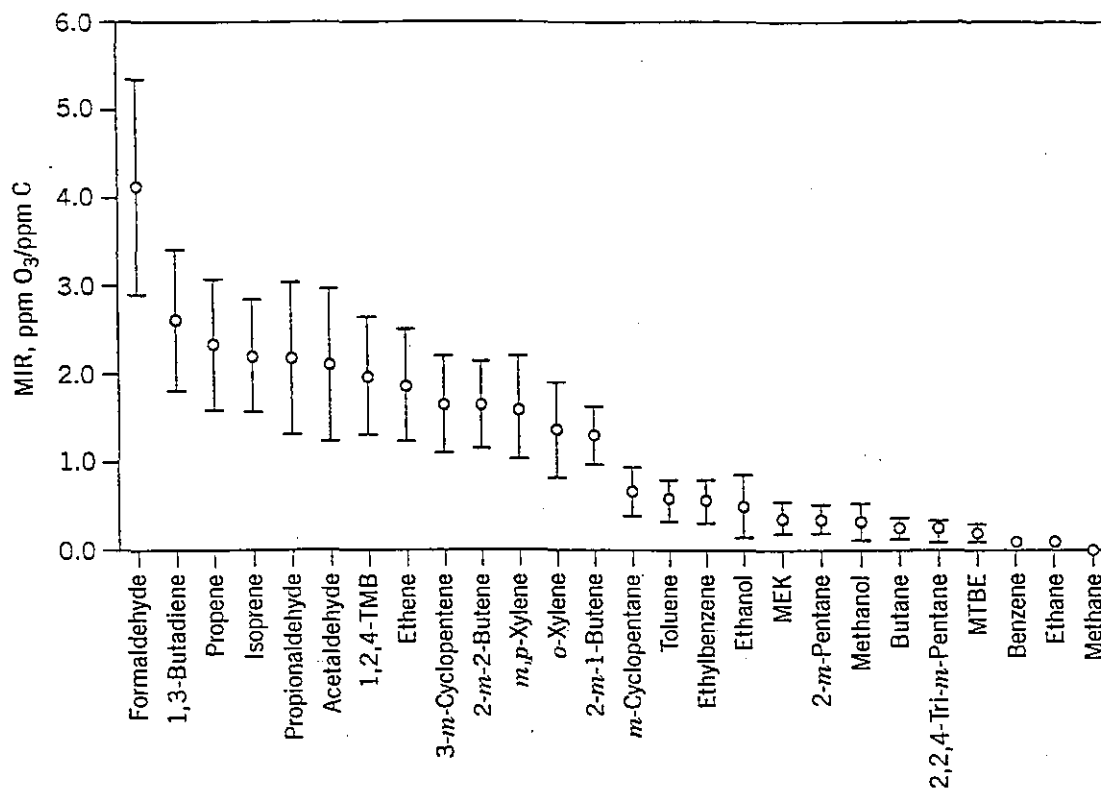


Figure 8. Mean values and  $1\sigma$  uncertainties of MIRs for selected organic compounds, as calculated from uncertainties in kinetic parameters (84).

tests on a small number of vehicles, particularly for the AFVs (92,111,112). Further, there is relatively little information on the effect of deterioration on the species emitted. More tests across a wide range of vehicles are required to better characterize the impact of uncertainty in fuel composition on calculation of RAFs.

Additionally, automobile source emissions are better characterized than most other sources. Although lack of detailed knowledge on the emissions compositions of various types of sources does add uncertainty to control strategy design, regulations that explicitly credit industry for emitting less reactive compounds could add a valuable economic incentive for more completely characterizing source emissions, particularly for the largest emitters. This has already been the case for automotive emissions. This emissions composition information would be useful for better evaluating the efficacy of controls and for other studies that depend on an accurate knowledge of emissions compositions, such as receptor modeling studies to help characterize emissions inventories.

#### OZONE REDUCTION THROUGH CONTROL STRATEGIES BASED ON VOC REACTIVITY

It has been recognized, primarily due to alternative fuel studies, that changing the reactivity of emissions could have positive air quality effects. This concept has been carefully considered for regulatory applications, and has resulted in the implemen-

tation of the California LEV/CF regulations focused on alternative transportation fuel use. A number of reactivity studies led to these regulations. The ozone reduction potential of methanol-fueled vehicles versus CFVs has been calculated and potential reductions have been found of 34% for an 85% methanol blend, and 86% for pure methanol. Using a three-dimensional urban airshed model, it was predicted (99) that pure methanol fuel use in the Los Angeles area in the year 2000 could lead to 16% decreases in peak ozone levels and 22% decreases in exposure levels if mass emissions were held constant.

This type of analysis makes clear that any reformulation strategies for mobile or stationary sources should account for the reactivity changes in the reformulated product. Otherwise, air quality may degrade. In the surface coatings industry, regulations to reduce VOC mass emissions have produced a shift from petroleum VOC solvent-borne coatings to low-volatility organic compound waterborne coatings. Organic cosolvents are still present in waterborne paints at low total VOC levels, and include ethylene glycol, propylene glycol, and glycol ethers. It remains an open question as to how reactive some of these newer organic cosolvents are relative to the petroleum distillates used in solvent-borne paints (114).

In current practice, the EPA uses a two-tiered reactivity scale, classifying compounds less reactive than ethane as unreactive, and the rest as reactive. For investigations of reactivity, the EPA primarily uses the  $k_{OH}$  scale, a scale based on OH rate constants. However, as discussed previously,

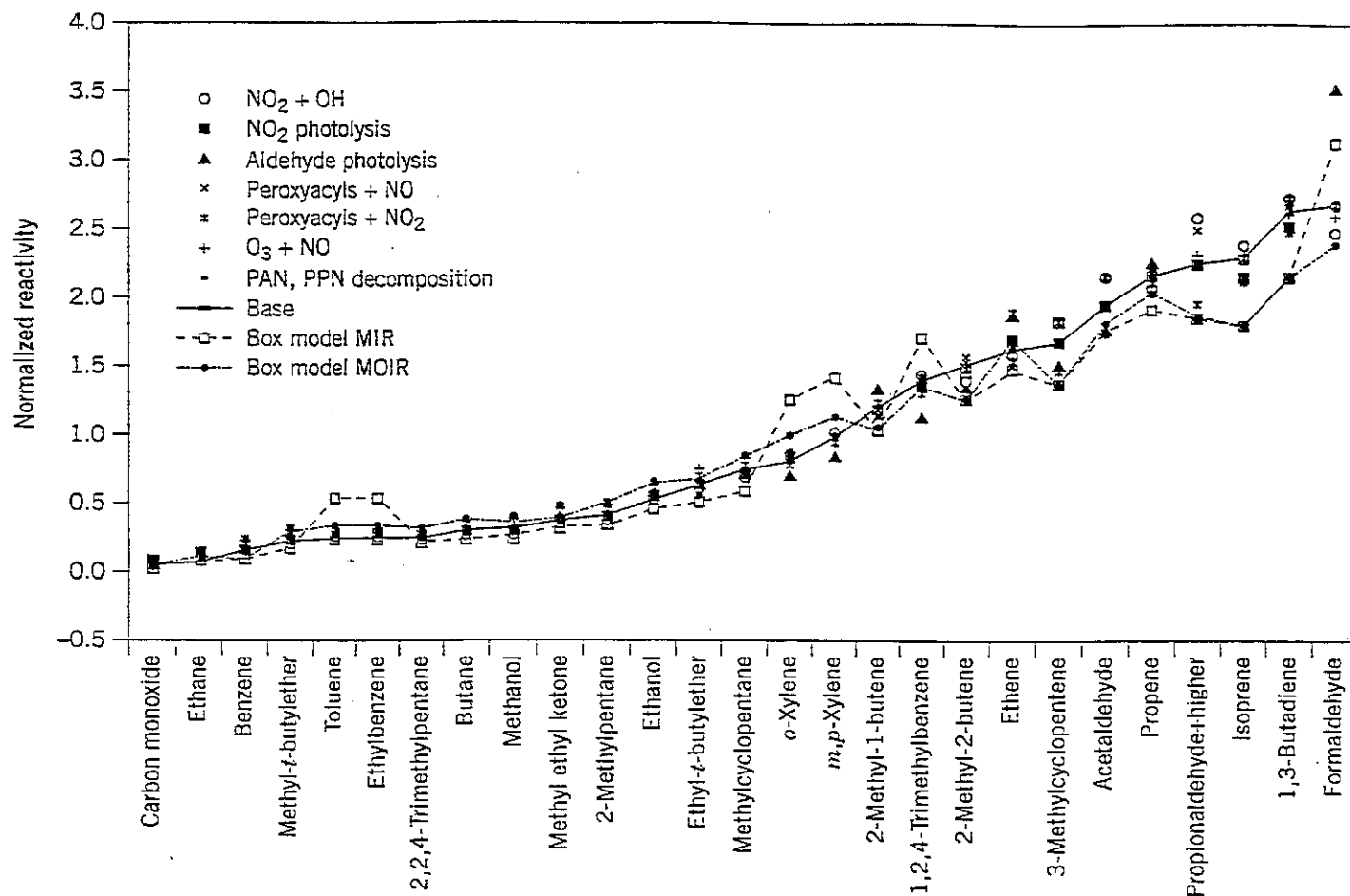


Figure 9. Spatial exposure reactivity predictions from rate-constant uncertainty adjustments (87).

this approach ignores the mechanistic aspects of ozone formation, because the initial  $\text{KOH}$  reaction rate may not accurately reflect subsequent photooxidation of products and overemphasizes the role of the most initially reactive species. In conjunction with efforts to develop regulations for VOC emissions for consumer products, the EPA has used the MIR scale to classify VOCs into three tiers: negligibly reactive (methane, ethane, halogenated organics), reactive (primarily alcohols), and highly reactive (115). However, the EPA recommends further research on the underlying science, and has not formalized a method to determine the bounds between reactivity groupings.

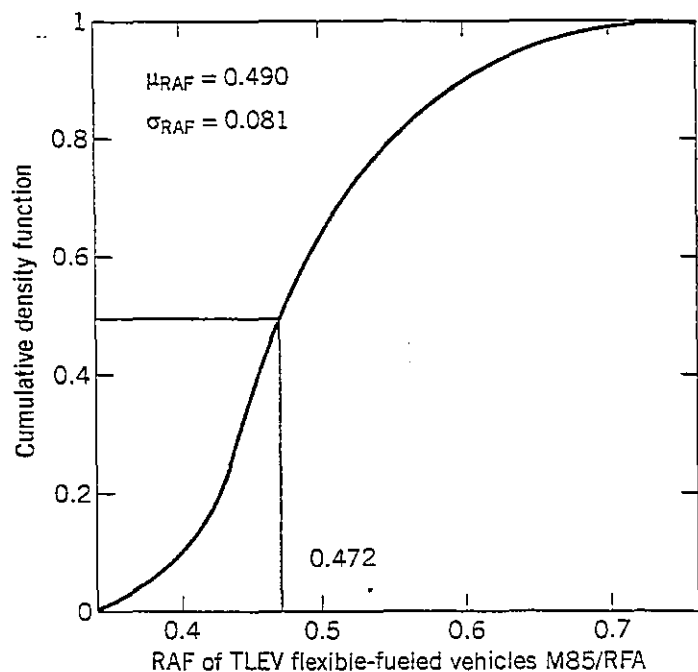
The California air regulators have been the most active state in promulgating reactivity-based regulations. CARB adopted vehicle regulations that are the first to use a detailed reactivity scale. The goal of the regulations is to use reactivity measures as a means to put alternative fuels on an equal regulatory playing field as conventional fuels with respect to urban ozone formation.

#### California's Motor Vehicle Regulations

In 1987, California Assembly Bill 234 created the Advisory Board on Air Quality and Fuels to evaluate and make recom-

mendations regarding the necessity and feasibility of using mandates or incentives to facilitate the introduction of cleaner transportation fuels in California. The statute assigned the Advisory Board the task of defining low-emission vehicles (LEVs) that either are fueled with conventional gasoline and meet a hydrocarbon exhaust emission standard half that otherwise applicable to light-duty vehicles, or operate on alternative fuels with an equivalent or lower impact on ozone. The AB234 Advisory Board (116) concluded that increased use of cleaner fuels can be achieved by adopting air quality-based performance standards using fuel-pool averaging. The staff of CARB (62) recommended that regulations use the reactivity of vehicle exhaust as the basis to compare the air quality impacts of various fuels.

In September 1990, CARB (24) implemented the recommendations of the AB234 Advisory Board by adopting the LEV/CF regulations, which introduced RAFs (as discussed previously). The California regulations specify the use of the MIR scale to calculate the RAFs because it was determined to be the most appropriate reactivity scale to complement California's  $\text{NO}_x$  control program. Nitrogen oxide controls are being implemented to reduce ozone under conditions that are sensitive to  $\text{NO}_x$  (generally downwind of emission source areas), and the organic gas controls are designed to reduce ozone under condi-

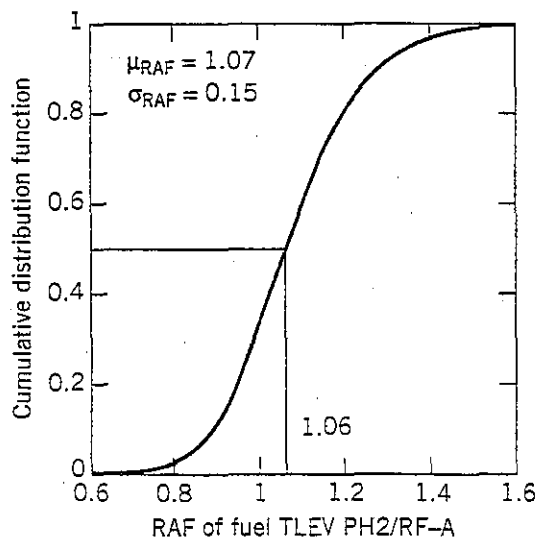


**Figure 10.** Mass-based cumulative distribution function of the uncertainty in the RAF of prototype flexible-fueled M85 vehicles (96).

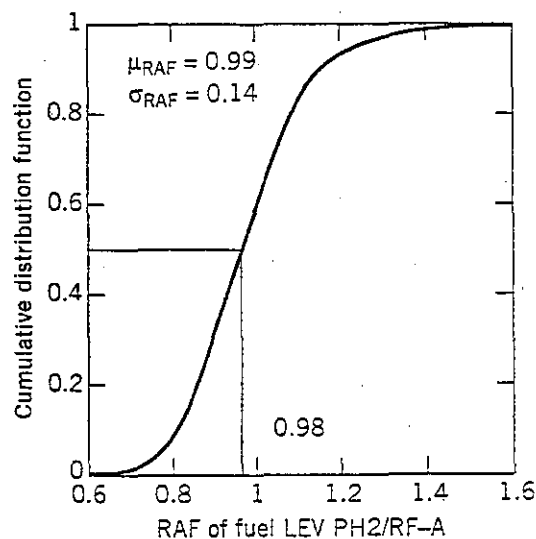
tions most sensitive to organic gases (generally near emission source areas). The NRC (2) has endorsed reactivity scaling as a valid way to treat fuels equally. Because of residual uncertainties in the chemical mechanisms used to calculate the reactivity scales, the MIR scale will be updated every three or more years using the mechanism best reflecting current knowledge.

The LEV/CF regulations require vehicle manufacturers to meet fleet average NMOG exhaust emission standards that begin at 0.250 g/mile in 1994 and are progressively reduced to a level of 0.062 g/mile in 2003. In addition to the LEV defined by AB234, the regulations establish four other classes of vehicles, with different standards for emissions of  $\text{NO}_x$ , NMOG, carbon monoxide (CO), and formaldehyde (HCHO). Transitional-low emission vehicles (TLEVs), LEVs, ultra-low emission vehicles (ULEVs), and zero emission vehicles (ZEVs) would certify at 50,000 miles to the standards presented in Table 13. Standards at 100,000 miles are slightly higher. Automobile manufacturers can use any combination of TLEVs, LEVs, ULEVs, ZEVs, and 1993 conventional vehicles to meet the fleet average standards. A separate requirement for the production of ZEVs begins in 2003. It is entirely up to the vehicle manufacturers whether to build cars powered with alternative fuels or not. The manufacturers received a reactivity credit for California's reformulated gasoline specifications, called Phase II gasoline, that went into effect in 1996.

To calculate RAFs, the full range of organic gases that contribute to ozone formation must be identified and quantified. Accordingly, the traditional nonmethane hydrocarbon (NMHC) standards are redefined in terms of NMOG, requiring the measurement of alcohols, aldehydes, and other oxygenated compounds. As described earlier, the emission rates of all NMOG species are converted to an appropriate mass of ozone using the MIR scale and are summed to estimate the reactivity of the entire exhaust sample. The new vehicle testing protocol, which involves detailed gas chromatographic analysis of hydrocarbon emissions and wet-chemical determinations of emissions of oxygenated compounds, is generally too time consuming and expensive to use in routine testing. This led CARB to adopt a two-part approach to enforcing the new motor vehicle emission standards; the RAFs are determined by speciated analysis of emissions for a small number of vehicles, and the reactivity-adjusted standards are enforced with more



(a)



(b)

**Figure 11.** Mass-based cumulative distribution functions for the RAFs of exhaust emissions associated with California gasolines: (a) TLEV Phase 2 to RFA (reformulated average gasoline) and (b) LEV Phase 2 to RF-A (83).

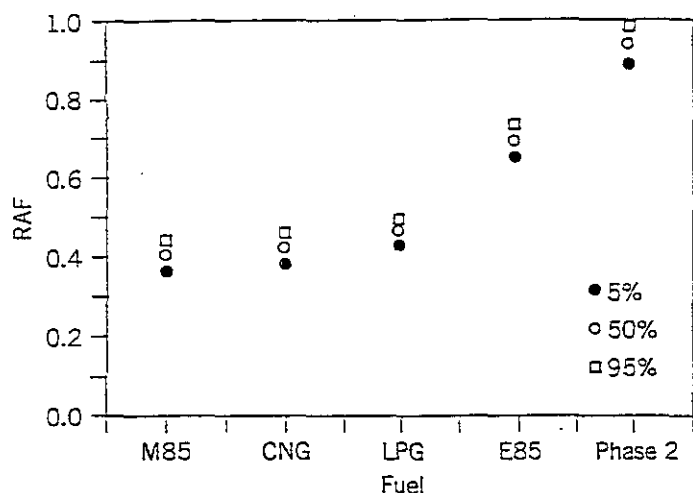


Figure 12. Variation in reactivity adjustment factors due to exhaust composition for four alternative fuels (5th, 50th, 95th percentiles shown) (96).

Table 13. Low-Emission Vehicle Exhaust Emission Standards for Passenger Cars at 50,000 Miles

Vehicle Category	Grams/Mile by Pollutant			
	NMOG <sup>a</sup>	NO <sub>x</sub>	CO	HC+CO
Current	0.390	0.4	7.0	None
1993 <sup>b</sup>	0.250	0.4	3.4	0.015 <sup>c</sup>
TLEV	0.125	0.4	3.4	0.015
LEV	0.075	0.2	3.4	0.015
ULEV	0.040	0.2	1.7	0.008
ZEV <sup>d</sup>	0.000	0.0	0.0	0.000

<sup>a</sup> NMHC for current and 1993 standards, NMOG with reactivity adjustment for others.

<sup>b</sup> Equivalent to Federal Tier I standards.

<sup>c</sup> Methanol-fueled vehicles only.

<sup>d</sup> Does not include power generation emissions.

routine measurements of total NMOG emissions for a larger number of vehicles. The procedure for determining the RAF for each type of alternative fuel vehicle is set forth in the California regulations (24). Manufacturers may determine RAFs for their specific engine families in accordance with this procedure, or they may use default RAFs established by the ARB. The lower levels of emissions, and the additional species that need to be measured, have provided stimulus for further development of automated analytical chemical techniques.

Although reactivity-based VOC controls are now established for motor vehicles, it is not certain whether they should be applied to stationary sources such as coatings, solvents, and consumer products. Although reactivity-based controls may potentially achieve greater VOC reductions than current mass-based controls, and the range of reactivities of stationary source emission is greater than those of fuels and vehicles, there are many unresolved concerns on emissions composition, MIR values, cost, and enforcement. One current initiative for stationary source controls is an investigation of whether a reactivity framework can be applied to the next generation of rule-making for consumer products and architectural coatings.

### Economic Benefits

An important question to address in regards to the use of reactivity quantification in regulations is whether its use would provide economic or environmental benefits. A mixed integer programming approach was applied to the optimization of ozone control strategies to determine if using reactivity quantification would provide economic benefits (117). In that study, using emission compositions and costs for the Los Angeles air basin, economically optimized VOC-based control strategies are determined using two approaches: one neglecting and one accounting for the reactivity differences of the mass emissions. In the first case, an optimized mass-based strategy is simulated such that the total VOC mass reductions are maximized at each cost level. Second, a reactivity based scheme is assumed in which the reactivity of each source's emissions are calculated and the ozone reductions are maximized at each cost level. Results from the two approaches are compared in Figure 13 for ozone reduction at a given expenditure level.

Figure 13 depicts the results for the optimization model across different levels of total cost. Optimal reductions for mass- and reactivity-based systems are scaled according to source reactivities. From this graph, it is clear that on an annual basis the reactivity-based system achieves the same ozone reductions at a lower total cost than the mass-based system. For example, at control costs of \$15 million per year, the ozone reduction achieved using a reactivity-based scheme is about twice that achieved under the mass-based scheme. As control costs escalate, the two methods converge, because a greater proportion of all sources will be controlled in both cases. Up to control levels of about 25% of the total controllable emissions, the reactivity-based scheme gives notably greater ozone reductions for the same cost. The graph does not converge at zero because of the inclusion of a category with a negative cost-effectiveness. CARB estimated a negative value of cost-effectiveness in this case due to anticipated savings from reformulation of a particular coatings process. Further economic benefits can accrue over time as control technologies are developed specifically for reactivity adjustment. Cities

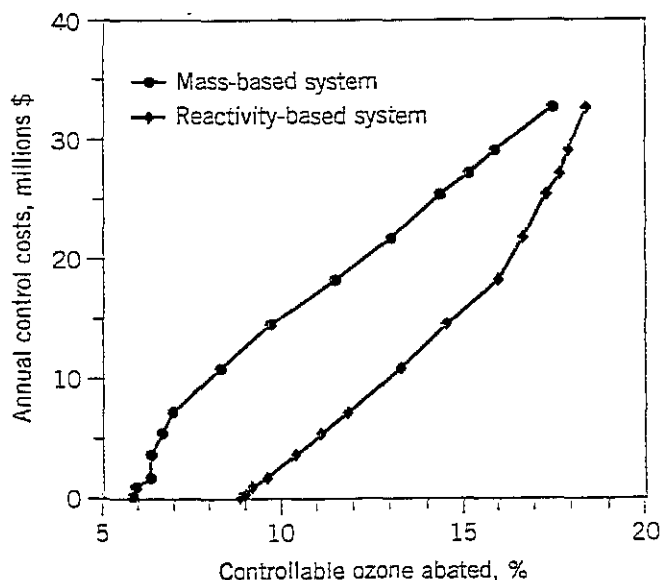


Figure 13. Percent of controllable ozone abated at different levels of total control cost (117).

that can best use such strategies include those areas where ozone formation is VOC-limited, as is suggested is the case for the coastal California cities, Phoenix, and Chicago. Another application of reactivity quantification to lower total control costs is as a basis for VOC emissions trading between sources. Without a sound foundation for quantifying the impact of one source's emissions compared to another, it is difficult to ensure that a VOC trade would not adversely affect air quality.

The use of reactivity adjustments in control strategy design allows a new avenue for air quality improvement. Reactivity-based control strategies can include economic incentives which would ensure that reformulation would lower reactive VOCs and improve air quality. Today's mass-based regulations credit industry for reducing tons of all VOCs, rather than reductions in the most reactive compounds. A hidden problem in reformulation regulations, familiar to the surface coating and consumer products industries, is that although the reformulated product may emit less mass of VOCs, the composition of the emissions may lead to greater ozone formation. Thus, the cost to reformulate may not necessarily pay off in improved air quality. By creating a regulatory structure that would promote selective control of VOCs with higher reactivity, reformulation and other control technologies can be evaluated and developed with respect to tradeoffs between reactivity and mass of emissions, leading to pollution prevention through more cost-effective process and product design.

As discussed, there are a variety of economic and environmental reasons to use VOC reactivity. What is less clear are the regulatory burdens this may entail. For example, accounting for reactivity causes a greater need to know the composition of emissions, which has an associated cost. Reference methods would need to be developed. Further, assuming that the composition is determined by the source industry, regulatory oversight may be challenging. Issues regarding industrial secrets (eg, product compositions) have also been raised. These questions should be addressed in conjunction with the implementation of any wide-ranging reactivity-based policy aimed at reducing urban ozone.

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#### BIBLIOGRAPHY

1. J.H. Seinfeld, *Atmospheric Chemistry and Physics of Air Pollution*, John Wiley & Sons, Inc., New York, 1986, pp. 36-42.
2. National Research Council *Rethinking the Ozone Problem in Urban and Regional Air Pollution*, National Academy Press, Washington, D.C. 1991.
3. J. Fishman, *Global Consequences of Increasing Tropospheric Ozone Concentrations*, National Air and Space Association, Langley Research Center, Hampton, Va., NAS 1.15:103477 and NASA-TM-103477, Feb., 1989.
4. Centers for Disease Control and Prevention. *JAMA*, 273(19), 1484-1485 (May 1995).
5. U.S. Congress, Office of Technology Assessment. *Catching Our Breath: Next Steps for Reducing Urban Ozone*, OTA-O-412, U.S. Government Printing Office, Washington, D.C. 1989.
6. S.M., Horvath, and D.J. McKee, In *Tropospheric Ozone: Human Health and Agricultural Impacts*, D.J. McKee, ed., CRC Press/Lewis Publishers, Boca Raton, Fla., 1994, Chapt. 3.
7. M. Lippmann, *Environ. Sci. Technol.* 25(12), 1954-1962 (1991).
8. M. Lippmann, *J. Exp. Anal. Environ. Epidemiol.* 3(1), 103-129 (1993).
9. W.L. Chameides, P.S. Kasibhatla, J. Yienger, and H. Levy. *Science*, 264(5155), 74-77 (Apr. 1994).
10. D.T. Tingey, D.M. Olszyk, A.A. Herstrom, and E.H. Lee, "Effects of Ozone on Crops," in D.J. McKee, ed., *Tropospheric Ozone: Human Health and Agricultural Impacts*, CRC Press/Lewis Publishers, Boca Raton, Fla., 1994, Chapt. 6.
11. S.B. McLaughlin, and L.J. Downing, *Nature* 374(6519), 252-254 (1995).
12. W. Mehlhorn, *Nature*, 327, 417 (1989).
13. Environmental Protection Agency, *Review of the NAAQS for Ozone*, Clean Air Scientific Advisory Committee, Washington, D.C., EPA-SAB-CASAC-89-1092, 1989.
14. U.S. EPA, "EPA Announces 96 Areas Failing to Meet Smog Standards," Office of Public Affairs, Washington, D.C., Aug. 1990.
15. B. Oulrey, personal communication, California Air Resources Board, Sacramento, Calif., Feb. 29, 1996.
16. South Coast Air Quality Management District 1997 *Air Quality Management Plan*, Nov. 1996.
17. J.A. Logan, M.J. Pather, S.C. Wofsy, and M.B. McElroy, *J. Geophys. Res.*, 86, 7210-7254 (1981).
18. F.W. Lurmann, and H.H. Main, *Analysis of the Ambient VOC Data Collected in the Southern California Air Quality Study*, Final Report, Contract A832-130, California Air Resources Board, Sacramento, Calif., 1992.
19. F.M. Bowman, and J.H. Seinfeld, *J. Geophys. Res.*, 99, 5309-5324 (1994).
20. R. Atkinson, *Atmos. Environ.*, 24A, 1-24 (1990).
21. R. Atkinson, *J. Phys. Chem. Ref. Data*, Monograph No. 2 (1994).
22. W.P.L. Carter, and R. Atkinson, *Environ. Sci. Technol.*, 23, 864 (1989).
23. W.P.L. Carter, *J. Air Waste Mgmt. Assoc.*, 44, 881-899 (1994).
24. CARB *Proposed Regulations for Low-Emission Vehicles and Clean Fuels—Staff Report and Technical Support Document*, Sacramento, Calif., August 13, 1990. See also Appendix VIII of *California Exhaust Emission Standards and Test Procedures for 1988 and Subsequent Model Passenger Cars, Light Duty Trucks and Medium Duty Vehicles*, as last amended Sept. 22, 1993. Incorporated by reference in Section 1960.1(k) of Title 13, California Code of Regulations.
25. M.C. Dodge, "Combined Use of Modeling Techniques and Smog Chamber Data to Drive Ozone-Precursor Relationships" in

- Proceedings, International Conference on Photochemical Oxidant and Its Control*, Research Triangle Park, N.C., EPA-600/3-80-028a, 1977.
26. G.L. Gipson, *Users Manual for OZIPM-2: Ozone Isopleth Plotting Package with Optional Mechanism / Version 2*, EPA/450/4-84-024, Aug. 1984.
  27. S.D. Reynolds, P.M. Roth, and J.H. Seinfeld, *Atmos. Environ.*, **7**, 1033-1061 (1973).
  28. S.D. Reynolds, T.W. Tesche, and L.E. Reid, *An Introduction to the SAI Airshed Model and its Usage*, San Rafael, Calif., Systems Application Inc., Report No. RTI/3999/18-04F, 1979.
  29. G.J. McRae, W.R. Goodin, and J.H. Seinfeld, *Mathematical Modeling of Photochemical Air Pollution*, EQL Report No. 18, Final Report to the State of California Air Resources Board, 1982.
  30. R.A. Harley, A.G. Russell, G.J. McRae, G.R. Cass, and J.H. Seinfeld, *Environ. Sci. Technol.* **27**, 378-388 (1993).
  31. R.J. Yarmartino, J.S. Scire, S.R. Hanna, G.R. Carmichael, and Y.S. Chang, *CALGRID: A Mesoscale Photochemical Grid Model, Volume 1: Model Formulation Document*, Final report on Contract A6-215-74 for the California Air Resources Board, Sacramento, Calif., 1989.
  32. R.J. Yarmartino, J.S. Scire, G.R. Carmichael, and Y.S. Chang, *Atmos. Environ.*, **26A**, 1493-1512 (1992).
  33. R.G. Lamb, *Regional Scale (1000 km) Model of Photochemical Air Pollution, Part 1. Theoretical Formulation*, EPA/600/3-83-035, U.S. Environmental Protection Agency, Environmental Sciences Research Laboratories, Research Triangle Park, N.C., 1983.
  34. R.L. Dennis, D.W. Byun, J.H. Novak, K.J. Galluppi, C.J. Coats, and M.A. Vouk, *Atmos. Environ.* **30**(12), 1925-1938 (1996).
  35. W.P.L. Carter, *Atmos. Environ.*, **24A**, 481-518 (1990).
  36. M.W. Gery, G.Z. Whitten, and J.P. Killus, *J. Geophys. Res.* **94**, 12925-12956 (1989).
  37. F.W. Lurmann, W.P.L. Carter, and R.A. Coyner, *A Surrogate Species Chemical Reaction Mechanism for Urban-Scale Air Quality Simulation Models, Volume I, Adaptation of the Mechanism*, EPA-600/3-87-014a, 1987.
  38. W.R. Stockwell, P. Middleton, J.S. Chang, and X. Tang, *J. Geophys. Res.*, **95**, 16343-16376 (1990).
  39. R.G. Derwent, and A.M. Hov, *Computer Modeling Studies of Photochemical Air Pollution Formation in North West Europe*, AERE R 9434, Harwell Laboratory, Oxfordshire, U.K., 1979.
  40. W.P.L. Carter, *Atmos. Environ.*, **29**, 2513-2517 (1995).
  41. W.P.L. Carter, D. Luo, L.L. Malkina, and D. Fitz, *The University of California, Riverside Environmental Chamber Data Base for Evaluating Oxidant Mechanism. Indoor Chamber Experiments through 1993*, Report submitted to the U.S. Environmental Protection Agency, EPA/AREAL, Research Triangle Park, N.C. March 20, 1995.
  42. H.E. Jeffries, R.M. Kamens, K.G. Sexton, and A.A. Gerhardt, *Outdoor Smog Chamber Experiments to Test Photochemical Models*, EPA-600/3-82-016a, Apr. 1982.
  43. S.C. Wang, R.C. Flagan, and J.H. Seinfeld, *Atmos. Environ.*, **26A**, 421-434 (1992).
  44. J.R. Odum, T. Hoffmann, F. Bowman, D. Collins, R.C. Flagan, and J.H. Seinfeld, *Environ. Sci. Technol.*, **30**, 2580-2585 (1996).
  45. N.A. Kelly, P. Wang, S.M. Japar, M.D. Hurley, and T.J. Wallington, *Measurement of the Atmosphere Reactivity of Emissions from Gasoline and Alternative-Fueled Vehicles: Assessment of Available Methodologies*, First-Year Final Report, CRC Contract No. AQ6-1-92, Coordinating Research Council, Atlanta, Ga., 1994.
  46. N.A. Kelly, and P. Wang, *Part I: Indoor Smog Chamber Study of Reactivity in N.A. Kelly, P. Wang, S.M. Japar, M.D. Hurley, and T.J. Wallington, Measurement of the Atmosphere Reactivity of Emissions from Gasoline and Alternative-Fueled Vehicles: Assessment of Available Methodologies*, Second-Year Final Report, CRC Contract No. AQ-6-1-92 and NREL Contract No. AF-2-11296-1, Coordinating Research Council, Atlanta, Ga., Sept. 1996.
  47. M.W. Gery, R.D. Edmond, and G.Z. Whitten, *Tropospheric Ultraviolet Radiation. Assessment of Existing Data and Effects on Ozone Formation*, Final Report, EPA-600/3-87-047, Oct. 1987.
  48. W.P.L. Carter, and F.W. Lurmann, *Evaluation of the RADM Gas-Phase Chemical Mechanism*, Final Report, EPA-600/3-90-001, 1990.
  49. W.P.L. Carter, and F.W. Lurmann, *Atmos. Environ.*, **25A**, 2771-2806 (1991).
  50. H.E. Jeffries, M.W. Gery, and W.P.L. Carter, *Protocol for Evaluating Oxidant Mechanisms for Urban and Regional Models*, Report for U.S. Environmental Protection Agency Cooperative Agreement No. 815779, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, N.C., 1992.
  51. W.P.L. Carter, and R. Atkinson, *Environ. Sci. Technol.*, **21**, 670-679 (1987).
  52. W.P.L. Carter, J.A. Pierce, L. Malkina, D. Luo, and W.D. Long, *Environmental Chamber Studies of Maximum Incremental Reactivities of Volatile Organic Compounds*, Report to Coordinating Research Council, Project No. ME-9; California Air Resources Board, Contract No. A032-0692; South Coast Air Quality Management District, Contract No. C91323; United States Environmental Protection Agency, Cooperative Agreement No. CR-814396-01-0; University Corporation for Atmospheric Research, Contract No. 59166; and Dow Corning Corporation, April 1, 1993.
  53. W.P.L. Carter, J.A. Pierce, D. Luo, and L.L. Malkina, *Atmos. Environ.*, **29**, 2499-2511 (1995).
  54. W.P.L. Carter, R. Atkinson, A.M. Winer, and J.N. Pitts, Jr., *Int. J. Chem. Kinet.*, **14**, 1071, (1982).
  55. K.W. Wilson, and G.J. Doyle, *Investigation of Photochemical Reactivities of Organic Solvents*, Final Report, SRI Project PSU-8029, Stanford Research Institute, Irvine, Calif., Sept. 1970.
  56. A.P. Altschuler, and J.J. Bufalini, *Environ. Sci. Technol.*, **5**, 39 (1971).
  57. J.L. Laity, F.G. Burstain, and B.R. Appel, *Adv. Chem. Series*, **124**, 95 (1973).
  58. J.J. Bufalini, T.A. Walter, and M.M. Bufalini, *Environ. Sci. Technol.*, **11**, 1181-1185 (1977).
  59. S.B. Joshi, M.C. Dodge, and J.J. Bufalini, *Atmos. Environ.*, **16**, 1301-1310 (1982).
  60. H.E. Jeffries, and K.G. Sexton, *The Relative Ozone Forming Potential of Methanol Fueled Vehicle Emissions and Gasoline-Fueled Vehicle Emissions in Outdoor Smog Chambers*, Draft Final Report to the Coordinating Research Council, Project No. ME-1, Sept. 1993.
  61. K.R. Darnall, A.C. Lloyd, A.M. Winer, J.N. Pitts, Jr., *Environ. Sci. Technol.*, **10**, 692 (1976).
  62. CARB *Definition of a Low-Emission Motor Vehicle in Compliance with the Mandates of Health and Safety Code Section 39037.05 (Assembly Bill 234, Leonard, 1987)*, Report by Mobile Sources Division, California Air Resources Board, El Monte, Calif., 1989.
  63. W.L. Chameides, F. Fehsenfeld, M.O. Rodgers, C. Cardelino, J. Martinez, D. Parrish, W. Lonneman, D.R. Lawson, R.A. Rasmussen, P. Zimmerman, J. Greenburg, P. Middleton, and T. Wang, *J. Geophys. Res.*, **97**, 6037 (1992).
  64. R. Atkinson, *Int. J. Chem. Kinet.*, **19**, 799-828 (1987).
  65. R. Atkinson, *J. Phys. Chem. Ref. Data*, Monograph No. 1. (1989).

66. F.M. Bowman, and J.H. Seinfeld, *Atmos. Environ.*, **28**, 3359-3368 (1994).
67. F.M. Bowman, and J.H. Seinfeld, *Prog. in Energy and Comb. Sci.*, **21**, 387-417 (1995).
68. M.C. Dodge, *Atmos. Environ.*, **18**, 1657 (1984).
69. W.P.L. Carter, *Development of Ozone Reactivity Scales for Volatile Organic Compounds*, EPA 600/3-91-050, U.S. Environmental Protection Agency, Research Triangle Park, N.C., Aug. 1991.
70. B.R. Weir, A.S. Rosenbaum, L.A. Gardner, G.Z. Whitten, and W. Carter, *Architectural Coatings in the South Coast Air Basin: Survey, Reactivity, and Toxicity Evaluation*, Final Report to the South Coast Management District, SYSAPP-88/137, Systems Applications, Inc., San Rafael, Calif., Dec. 1988.
71. T.Y. Chang, and S.J. Rudy, *Atmos. Environ.*, **24A**(9), 2421-2430 (1990).
72. W.P.L. Carter, D. Luo, L.L. Malkina, and J.A. Pierce, *Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds, Effects of Varying ROG Surrogate and NO<sub>x</sub>*, Final report to Coordinating Research Council, Inc., Project ME-9, California Air Resources Board, Contract A032-0692, and South Coast Air Quality Management District, Contract C91323, March 24, 1995.
73. H.E. Jeffries, and R. Crouse, *Scientific and Technical Issues Related to the Application of Incremental Reactivity, Part H: Explaining Mechanism Differences*, Report prepared for Western States Petroleum Association, Glendale, Calif., Oct. 1991.
74. W.P.L. Carter, E. Luo, L.L. Malkina and J.A. Pierce, *Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds, Effects of Varying Chamber and Light Source*, Final report to National Renewable Energy Laboratory, Contract XZ-2-12075, Coordinating Research Council, Inc., Project M-9, California Air Resources Board, Contract A032-0692, and South Coast Air Quality Management District, Contract C91323, March 26, 1995.
75. H.E. Jeffries, K. Sexton, and J. Yu, *Atmospheric Photochemical Studies of Pollutant Emissions from Transportation Vehicles Operating on Alternative Fuels*, Draft final report to the National Renewable Energy Laboratory, Golden, Colo., April 1996.
76. W.P.L. Carter, University of California, Riverside, Calif., unpublished results, 1996.
77. T.E. Kleindienst, J.A. Stikeleather, C.O. Davis, D. Smith, and F. Black, *Photochemical Reactivity Studies of Emissions from Alternative Fuels*, Report to the National Renewable Energy Laboratory for Contract TS-2-1116-1 and to the Atmospheric Research and Exposure Assessment Laboratory of the U.S. EPA, NREL, Golden, Colo., Mar., 1996.
78. G. Johnson, *Explanatory Notes and Supplementary Materials*, bound papers and reports for workshop at U.S. Environmental Protection Agency, Research Triangle Park, N.C., Dec. 12-13, 1991.
79. M.D. Hurley, S.M. Japar, and T.J. Wallington, *Part II: Assessment of Airtrak as a Reactivity Analyzer*, in N.A. Kelly, P. Wang, S.M. Japar, M.D. Hurley, and T.J. Wallington, *Measurement of the Atmosphere Reactivity of Emissions from Gasoline and Alternative-Fueled Vehicles: Assessment of Available Methodologies*, Environmental Research Consortium, Second-Year Final Report for CRC Contract No. AQ-6-1-92 and NREL Contract No. AF-2-11296-1, Jan. 1996.
80. H.E. Jeffries, K. Sexton, C. Rigsbee, and W. Li, *Experimental and Theoretical Studies of Reactivity as a Conserved Property Using an Airtrak*, Draft final report to the Coordinating Research Council (project CRC-AQ-5-1) and the Western States Petroleum Association (project DF-304-06), June, 1996.
81. R.G. Derwent, and M.E. Jenkin, *Atmos. Environ.*, **25**(A), 1661-1673. (1991).
82. L. McNair, A. Russell, and M.T. Odman, *J. Air Waste Mgmt. Assoc.*, **42**, 174 (1992).
83. Y.-J. Yang, M. Das, J.B. Milford, M.S. Bergin, A.G. Russell, and W.R. Stockwell, *Quantification of Organic Compound Reactivities and Effects of Uncertainties in Rate Parameter, An Integrated Approach Using Formal Sensitivity and Uncertainty Analysis and Three Dimensional Air Quality Modeling*, Report prepared for the Auto/Oil Air Quality Improvement Research Program, Aug., 1994.
84. Y.-J. Yang, W.R. Stockwell, and J.B. Milford, *Environ. Sci. Tech.*, **29**(5), 1336-1345 (1995).
85. M.S. Bergin, A.G. Russell, and J.B. Milford, *Environ. Sci. Tech.*, **29**(12), 3029-3037 (1995).
86. W. Jiang, D.L. Singleton, M. Hedley, and R. McLaren, *Atmos. Environ.*, **31**(4), 627-638 (1996).
87. M.S. Bergin, A.G. Russell, and J.B. Milford, "Effects of Chemical Mechanism Uncertainties on the Reactivity Quantification of Volatile Organic Compounds Using a Three-Dimensional Air Quality Model," *Environ. Sci. Tech.*, (in press) 1998.
88. M. Kahn, Y.J. Yang, and A.G. Russell, "Reactivities of Organic Solvents: Comparison between Urban and Regional Domains," Paper No. WA-97-1540, Presented at the A&WMA Annual Meeting, Toronto, Canada, June 1997, Air & Waste Management Association, Pittsburgh, Pa.
89. W.P.L. Carter, *Development and Application of an Up-to-Date Photochemical Mechanism for Airshed Modeling and Reactivity Assessment*, Draft final report for California Air Resources Board, Contract No. A934-094, Apr. 26, 1993.
90. G.Z. Whitten, *Evaluation of the Impact of Ethanol Gasoline Blends on Urban Ozone Formation*, Systems Applications, Inc., San Rafael, Calif. SYSAPP-88/029, 1988.
91. K. Baugues, *Preliminary Planning Information for Updating the Ozone Regulatory Impact Analysis Version of EKMA*, Draft Document, Source Receptor Analysis Branch, Technical Support Division, U. S. Environmental Protection Agency, Research Triangle Park, N.C., Jan., 1990.
92. CARB, *Proposed Reactivity Adjustment Factors for Transitional Low-Emissions Vehicles—Staff Report and Technical Support Document*, Sacramento, Calif., Sept. 27, 1991.
93. AQIRP, *Reactivity Estimates for Reformulated Gasolines and Methanol/Gasoline Blends in Prototype Flexible/Variable Fuel Vehicles*, Technical Bulletin No. 7, Auto/Oil Air Quality Improvement Research Program, Available from the Coordinating Research Council, Atlanta, Ga., 1993.
94. Y. Andersson-Skold, P. Grenfelt, and K. Pleije, *J. Air Waste Mgmt. Assoc.*, **42**, 1152-1158. (1992).
95. M.W. Gery, and R.R. Crouse *User's Guide for Executing OZIPR*, Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, N.C., 1989.
96. A. Russell, J. Milford, M.S. Bergin, S. McBride, L. McNair, Y. Yang, W.R. Stockwell, and B. Croes, *Science* **269**, 491-495 (1995).
97. J.C. Trijonis, K.W. Arledge, *Utility of Reactivity Criteria in Organic Emission Control Strategies: Application to the Los Angeles Atmosphere*, EPA/600/3-78/019; TRW/Environmental Services, Redondo Beach, Calif. 1976.
98. T.Y. Chang, S.J. Rudy, G. Kuntasal, R.A. Gorse, Jr., *Atmos. Environ.*, **23**(8), 1629-1644 (1989).
99. A.G. Russell, D. St. Pierre, and J.B. Milford, *Science* **247**, 201-205 (1990).

100. L.A. McNair, A.G. Russell, M.T. Odman, B.E. Croes, and L. Kao, *J. Air Waste Mgmt. Assoc.*, 44, 900-907 (1994).
101. Y.-J. Yang, J.B. Milford, *Environ. Sci. Tech.*, 30(1), 196-203 (1996).
102. Y.-J. Yang, W.R. Stockwell, and J.B. Milford, *Environ. Sci. Tech.*, 30(4), 1392-1397 (1996).
103. M.S. Bergin, A.G. Russell, Y.J. Yang, J.B. Milford, F. Kirchner, and W.R. Stockwell, *Effects of Uncertainty in SAPRC90 Rate Constants and Product Yields on Reactivity Adjustment Factors for Alternately Fueled Vehicle Emissions*, Report to the National Renewable Energy Laboratory, Golden, Colo., 80401, NREL/TP-425-7636, July 1996.
104. P.D. Guthrie, M.P. Ligocki, R.E. Looker, and J.P. Cohen, *Air Quality Effects of Alternative Fuels*, Phase 1, Draft Final Report for Subcontract 14072-02 to the National Renewable Energy Laboratory, Golden, Colo., Dec. 1996.
105. M.W. Gery, G.Z. Whitten, and J.P. Killus, *Development and Testing of the CBM-IV for Urban and Regional Modeling*, EPA-600/3-88-012, Jan. 1988.
106. G. Yarwood, System Applications, Inc., San Rafael, Calif., personal communication with W.P.L. Carter, 1994.
107. W.P.L. Carter, *Calculation of Reactivity Scales Using an Updated Carbon Bond IV Mechanism*, Draft Report prepared for Systems Applications International under funding from the Auto/Oil Air Quality Improvement Research Program, Apr. 12, 1994.
108. W.R. Stockwell, Y.-J. Yang, and J.B. Milford, *A Compilation of Estimated Uncertainty Factors for Rate Constants in W.P.L. Carter's Detailed Mechanism*, Report to the Auto/Oil Air Quality Improvement Research Program, CRC, Atlanta, Ga., 1994.
109. W.B. DeMore, S.P. Sander, D.M. Golden, M.J. Molina, R.F. Hampson, M.J. Durylo, C.J. Howard, and A. R. Ravishankara, *Chemical Kinetics Data for Use in Stratospheric Modeling, Evaluation No. 9*; National Aeronautics and Space Administration, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, Calif., 1990.
110. V.R. Burns, J.D. Benson, A.M. Hochhauser, W.J. Koehl, W.M. Dreucher, and R.M. Reuter, *Description of the Auto/Oil Air Quality Improvement Research Program*, SAE technical paper No. 912320, Society of Automotive Engineers, Warren, Pa., 1991.
111. CA EPA, "Preliminary Reactivity Adjustment Factors," State of California Environmental Protection Agency, 1995.
112. CARB, *Public hearing to consider amendments to certification requirements and procedures for low-emission passenger cars, light duty trucks and medium duty vehicles-supporting documents and information*, Sacramento, Calif., Mar. 1993.
113. V.R. Bishop, S.E. Fienberg, and P.W. Holland, *Discrete Multivariate Analysis: Theory and Practice*, MIT Press, Cambridge, Mass., 1975.
114. R.A. Harley, M.P. Hannigan, and G.R. Cass, *Environ. Sci. Technol.* 26(12), 2395-2408 (1992).
115. B. Dimitriadis, *J. Air Waste Manag. Assoc.*, 46(10), 963-970 (1996).
116. California Advisory Board on Air Quality and Fuels, *Report to the California Legislature*, Volume 1-Executive Summary, Oct. 2, 1989.
117. S. McBride, M. Oravetz, and A. Russell, *Environ. Sci. Tech.*, 31(5), 238A-244A (1996).